THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLIX FEBRUARY 1954 No. 2

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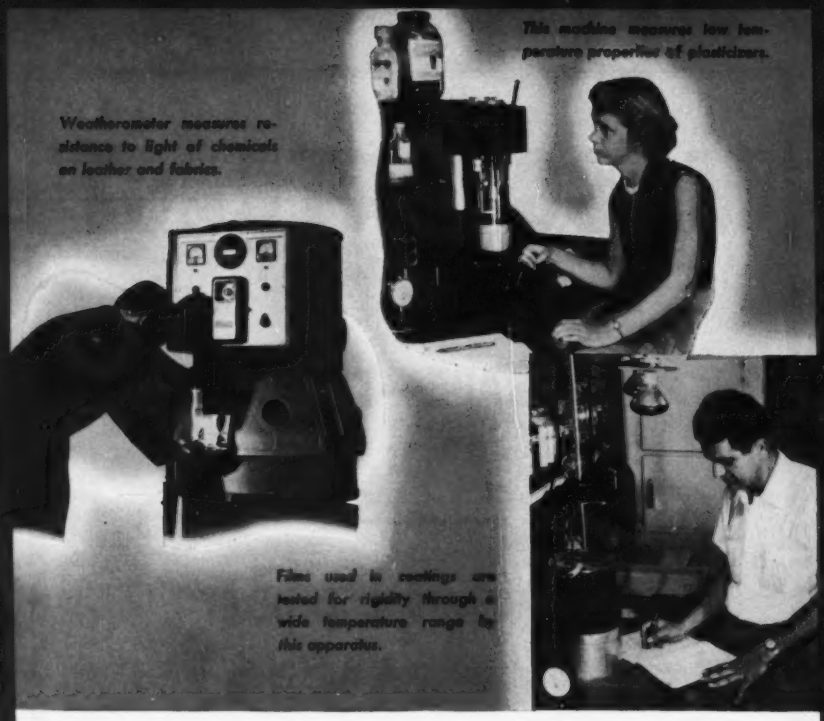
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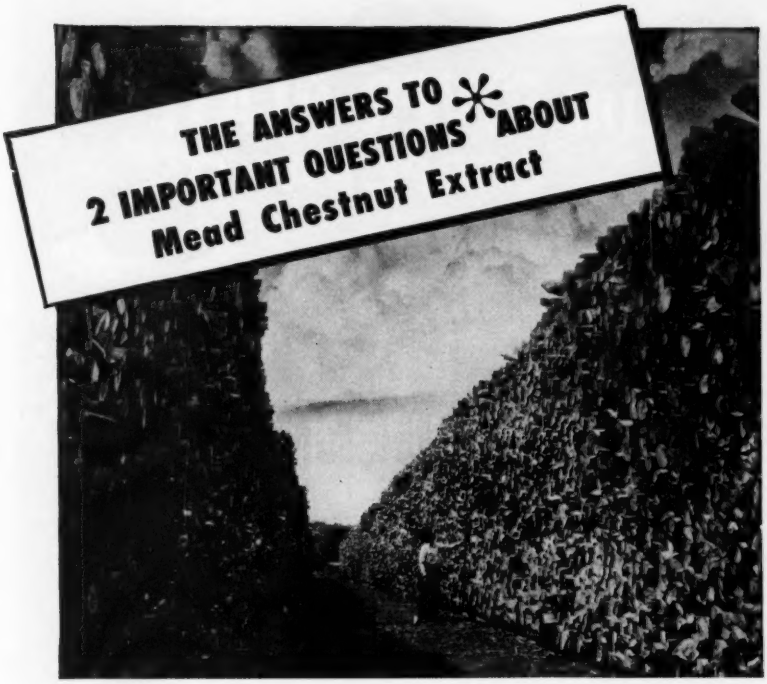

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*** 1. Is the supply of Mead Chestnut Extract adequate?**

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B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

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IT'S A FACT!

Mead Chestnut Extract will produce more pounds of plump leather per unit of tannin than any other tanning material.

Vegetable Tannin	Tan Yard Yield (white weight basis)
Chestnut Wood Extract	67%
Tanning Material A	61%
Tanning Material B	63%

Calculate your tanning material costs on a leather basis as well as on a tan unit basis. Mead Chestnut Extract, producing four to six pounds more leather, means positive savings.

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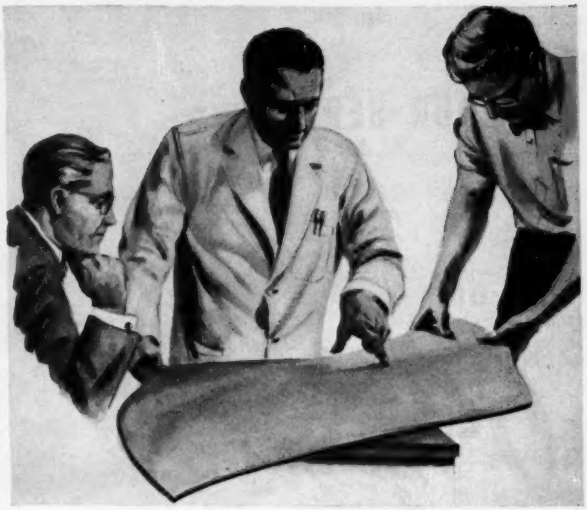

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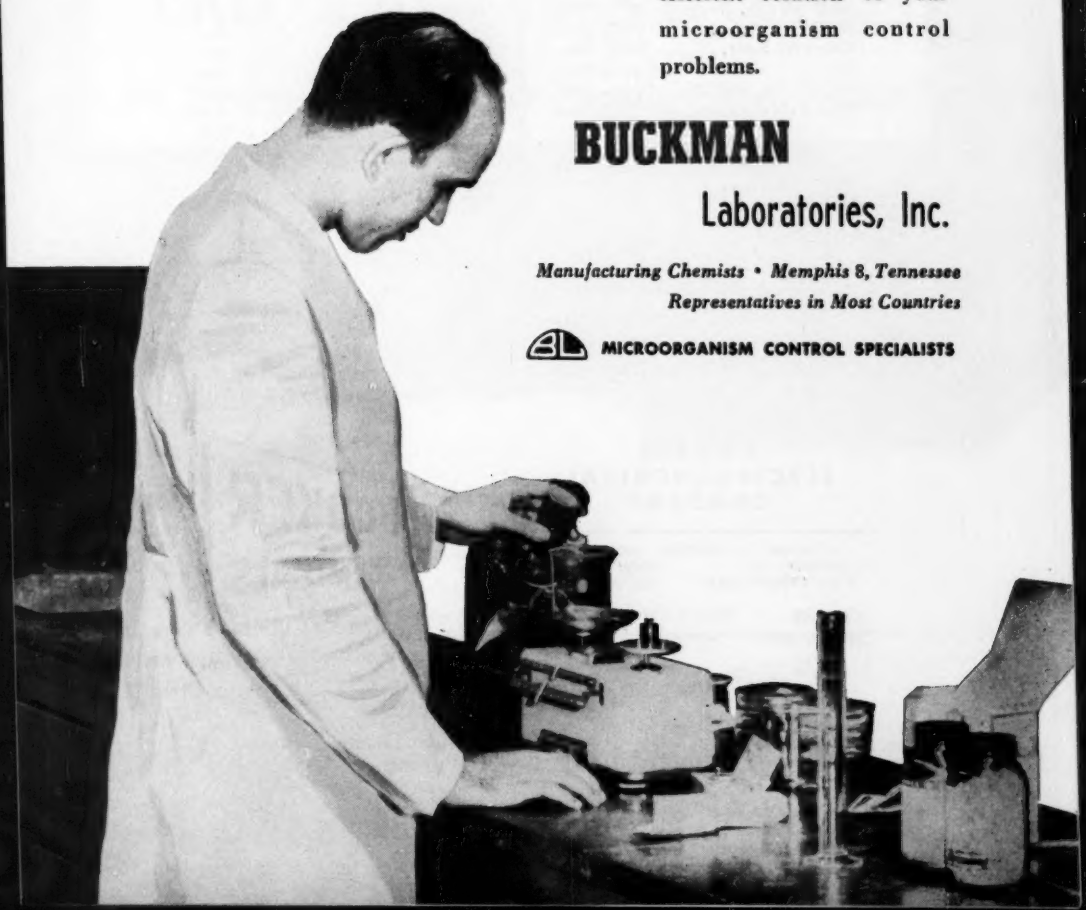

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Mol. Wt. 78.1
M.P. ..... 100°C

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ANALYSIS

Na_2S	60 to 62%
NaCl	1.5% Max.
Other Na Salts	2.0% Max.
Fe	8 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	35% Min.

SHIPPING CONTAINERS

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(sodium hydrosulfide)

Mol. Wt. 56.1
M.P. ..... 55°C

Light lemon colored solid in flake form. Completely and rapidly soluble in water, alcohol and ether.

ANALYSIS

NaSH	70 to 72%
Na_2S	2.5% Max.
NaCl	0.8% Max.
Na_2SO_3 and $NaHCO_3$	0.4% Max.
Fe	5 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	28 to 26%

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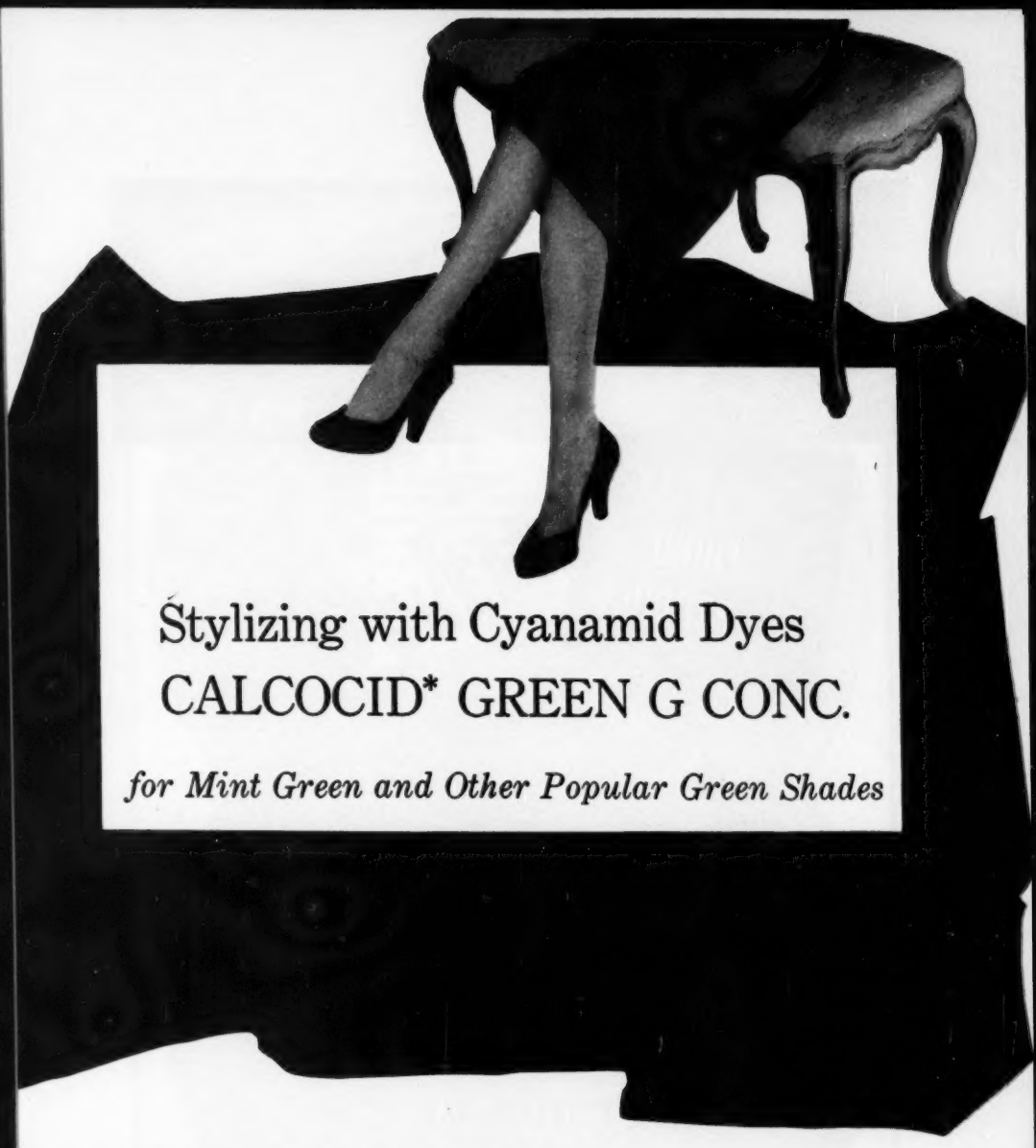

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VOL. XLIX FEBRUARY 1954 No. 2

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CONVENTION PAPERS

The Chairman of the Convention Committee, Dominic Meo, requests that the titles and abstracts of papers to be presented at the Bedford Meeting be submitted to him by March 1st. It is necessary for the Chairman to have this advance information for the preparation of the program.

MINUTES OF A MEETING OF DELEGATES OF THE INTERNATIONAL UNION OF LEATHER CHEMISTS SOCIETIES

Held at the University, Barcelona on Tuesday, Sept. 15th, 1953.

Minutes. The minutes of the London 1951 meeting were read by the Secretary, summarized in French by the President and accepted.

Secretary's Report. The Secretary read his report of the activities of the Union since 1951. After being summarized in French by the President, it was approved.

Admission of Austria. The admission of the Austrian Leather Chemists Society was unanimously approved. Prof. Sagoschen said he much appreciated his Society being elected, and would do all possible to further the aims of the Union. Prof. Grassman said he too was pleased, because the German and Austrian Societies were in close contact.

Financial Statement. In the absence of the Hon. Treasurer, Prof. Burton, the balance sheet was presented by the Hon. Secretary. This was approved, and thanks expressed to the Hon. Treasurer for his work.

Election of Officers. The Committee warmly approved the nomination of Dr. H. G. Turley as 1st Vice-President for 1954–5. and he was formally elected.

Dr. A. Engeler was re-elected a co-opted member of the Executive Committee, and Dr. W. Grassmann was elected as a co-opted member in place of Dr. Turley. Dr. Burton was re-elected Hon. Treasurer, and Mr. Harvey as Hon. Secretary for a further period of four years. Mr. Harvey being thanked for his services.

Mr. Harvey replied for both Prof. Burton and himself.

Dr. Gustavson said he felt honoured at being the next President and would fill the office to the best of his ability.

Mr. Mallebay said he was sorry to see Mr. Blockey depart from the Executive Committee, but he had worked very hard for the Union.

Venue of Conferencc 1955. Mr. Mallebay announced it had been decided to hold the 1955 Conference in Stockholm, Sweden.

A meeting of the Executive Committee of the International Union of Leather Chemists Societies was held at the Offices of the Spanish Leather Syndicate, Via Layetana 18, pral, Barcelona on Sunday Sept. 13th at 6 p.m.

Present: V. M. J. Mallebay (President) Dr. K. H. Gustavson, Mr. J. R. Blockey, Prof. D. Burton, Dr. A. Engeler. The Secretary, Mr. A. Harvey, was detained on account of train service. Dr. H. G. Turley sent a letter of apology for his absence.

The minutes of the London meeting, having been circulated were taken as read, accepted and signed by the President.

Secretary's Report. The Secretary's report for 1952-3 was read by the President and approved.

Austrian Society. The admission of the Austrian Leather Chemists Society was ratified.

Financial Statement. Prof. Burton read the financial statement which was approved. Arising from the financial statement it was agreed that the Secretary's Honorarium for the next two years be as in previous years. i. e. L25 per annum.

Election of Officers. It was unanimously agreed that Dr. H. G. Turley be elected 1st Vice-President for 1954-5, and this would be recommended to the Council of Delegates. The Hon. Treasurer and Hon. Secretary were re-elected.

Co-opted Members. It was proposed that Dr. A. Engeler be re-elected, and that Dr. W. Grassmann be elected co-opted members of the Executive Committee for 1954-5. This would be recommended to the Council of Delegates.

Conference 1955. It was decided that the 1955 Conference be held in Stockholm, and that the invitation of the Italian Society to hold a conference in Rome for 1957 be considered. It was further decided that the 1955 Stockholm Conference be held during the first or second week in August.

The General Secretary subsequently announced the election of Dr. H. G. Turley as first Vice-President for the years 1954-1955, following the recommendation of the Executive Committee as noted in the above minutes.

Hemlock Slabs as a Source of Pulp and Tannin*

NORMAN F. ROGER**, WALTER H. KOEPP*** and EDWARD L. GRIFFIN, JR.,**

*Eastern Regional Research Laboratory*****
Philadelphia 18, *Pennsylvania*

INTRODUCTION

In recent years considerable attention has been directed toward developing new sources of domestic vegetable tanning materials to replace chestnut

*This work is being done cooperatively by the Eastern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture, and the Michigan College of Mining & Technology.

**Eastern Regional Research Laboratory, Philadelphia 18, Pennsylvania.

***Michigan College of Mining & Technology, Houghton, Michigan.

****One of the Laboratories of the Bureau of Agricultureal and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

wood, which has been our principal domestic source but which is now disappearing due to the chestnut blight [1]. Our national defense authorities place vegetable tannin high on the list of critical materials necessary for a successful war effort. Should we in time of war be cut off from our main sources of supplies, our present domestic production would provide only a fraction of our needs. That fact, plus the marked downward trend in domestic production, is reason enough for sober concern.

To meet this deficit in domestic production, which still comes mainly from long-dead chestnut trees, investigators have proposed the utilization of scrub oaks in Florida [2], [3] and the mixed oaks of the Tennessee Valley [4], [5] as replacement sources of tannin. Other possible domestic sources proposed are the canaigre root [1] from the Southwest and bark from western hemlock [6] (Tsuga heterophylla (Raf.) Sarg.), Douglas fir, spruce and redwood of the West.

To this list of sources now being actively investigated should be added Eastern hemlock bark (Tsuga canadensis (L.) Carr.). (Perhaps it would be more accurate to say reinvestigated.) This is one of the oldest native sources of tannin in this country. [7]

In past years Michigan and Wisconsin have been important sources of peeled bark. Today this area alone supplies over 70 per cent of the hemlock cut in the eastern United States. It is estimated that the forests of Michigan and Wisconsin now contain about 1200 million cubic feet of hemlock with 75 per cent of this volume in Michigan. Fully 95 per cent of the hemlock growing in Michigan occurs in the Upper Peninsula. It is from this area that some 95 per cent of the peeled bark in the Lake States is produced. Thus our attention is directed to the Upper Peninsula of Michigan as the area that carries the greatest potential for any substantial increase in tannin production from hemlock bark in the eastern United States.

What are the reasons for the drop in consumption of hemlock bark from Michigan and Wisconsin within the last 25 years, from an estimated high of 63,000 cords in 1928 to some 4,400 cords in 1951? The main reason for this decline is that cost-conscious tanners have been able to secure other tanning materials at their plants for a lower cost per tan unit (1 pound of 100 per cent tannin) than from hemlock bark. Increasing freight charges and higher handling costs at the tanneries are both contributing to the unfavorable position of hemlock bark relative to other sources of vegetable tannins. As an example, the present delivered cost of a cord of bark from one of the important Upper Peninsula shipping points to a Lower Michigan tannery is $28.41 of which $11.41 is freight.

For the much longer freight hauls to tanneries in other states, delivered costs have made it economically impossible for some to continue using hemlock bark. Of the 36 companies in the United States who were the principal consumers of hemlock bark from Michigan and Wisconsin in the be-

ginning of the period between 1918 to 1952, only ten are still using bark. The others may either have discontinued operating or changed over to cheaper per unit cost foreign substitutes, mainly quebracho and wattle extracts.

It would seem from the foregoing that the only apparent solution to the problem of increased use of the hemlock tannin resource available in the Upper Peninsula of Michigan would be its production there as a liquid or possibly a powdered extract. It is to be noted that during World War I a 100-cord per day hemlock bark extract plant was operated successfully in conjunction with a modern tannery in the Upper Peninsula at Escanaba, Michigan. However, in the post-war depression that followed it was unable to compete with foreign extracts and barks and consequently was dismantled. Although it has been suggested a number of times, as far as we know no one has thoroughly evaluated the feasibility of such a proposal in the light of present day conditions. The Forest Products Research Division of the Michigan College of Mining and Technology at Houghton, Michigan, decided in 1949 to investigate the economics of hemlock tannin extract production in the Upper Peninsula.

The first phase of this investigation dealt with a study of the potential market for hemlock tannin extract. Of nine American firms contacted, six were primarily sole leather producers operating 21 tanneries, and the other three were engaged mainly in upholstery, baggage or upper leather production at their respective tanneries. This study indicated an anitial market for 5,000 tons of 100 per cent hemlock tannin in a price range of 18-22 cents per tan unit. Most of the firms contacted wished to tie the price they were willing to pay for hemlock tannin with the going market cost of quebracho extract.

Several experts in tannin extraction were contacted, and from the data they furnished hemlock extract production costs were estimated at 16–16-½ cents per tan unit based on a delivered bark cost of $17.00 per cord, open tank leaching and a recovery of 160 tan units per cord. The indicated profit margin of 1½–2 cents based on an 18 cent per tan unit f.o.b. price was too small in our opinion to interest any substantial capital investment in such an enterprise. The problem of economic feasibility thus resolves itself into whether or not extract costs can be reduced either by improvement in processing or by lowering the cost of the bark. No appreciable reduction in the cost of hand-peeled bark from pulp or sawmill logs can be anticipated unless the pulpmills can be persuaded to pay a greater differential for peeled logs than has been their custom.

Another possible source of bark in the Upper Peninsula is the large volume of sawmill slabs and edgings developed annually. Many portable sawmills have been forced to burn their slabs for lack of a profitable market. In the winter of 1950–51, 21 sawmills in the Upper Peninsula were contacted. Their hemlock lumber production for 1950 approximated 57 million board feet.

From U. S. Forest service data the total hemlock lumber production in the Upper Peninsula in 1950 was estimated to be 116 million board feet. The mills contacted thus covered 49 per cent of the production for that year. These operators were willing to sell some 36,000 cords at a nominal price (average $4.00) f.o.b. cars. The full potential in the Upper Peninsula that year based on 0.7 cord of slabs and edgings per M board feet would have been 81,200 cords. Of course, a fair percentage of these slabs would not be economically available.

These waste slabs contain 35–40 per cent bark and 65–60 per cent wood. The tannin content of the whole slabs including both bark and wood is too low for commercial tannin extraction and the bark content is too high for most pulping purposes. It is doubtful that the value of either of these fractions alone if segregated would be sufficient to pay for the segregation, but if both products could be obtained at a saleable purity, their segregation might be commercially feasible. Work was therefore initiated on these hemlock slabs to study methods of recovering both a high bark fraction suitable for extraction of tanning material and a wood fraction of sufficiently high wood content in a marketable form for pulping.

Our current thinking may be summed up in a proposal to collect slabs at a central point in the Upper Peninsula of Michigan, chip them, segregate the bark for use in an extract plant (50 cord per day capacity) at the same location and dispose of the "bark free" wood chips to pulpmills either in the Upper Peninsula or in nearby Wisconsin. The initial capacity of such a slab processing plant should be at least 100 cords per day for which there is an ample supply of slabs now and in the foreseeable future.

A chipping and bark segregation test on seasoned hemlock slabs is reported here.

Principles of the Process

Dunwody has described a method for producing pulp chips from unbarked logs [9].

The method of segregating bark and wood in chip form on an air flotation specific gravity separator reported by Calderwood and May [2] and later by Snow [4] appeared promising and was used in this study with some modifications. The application of this method requires the following:

1. There must be a sufficiently high "floatability" difference between the bark and wood chips.
2. The chipper must effect a high degree of detachment of bark and wood during chipping.
3. The chipper must produce wood chips with uniform fiber length acceptable for pulping operations and uniform bark chips with a low fines content suitable for extraction.

Specific gravity measurements made on several samples of bark and wood as well as the denser knots, reported in Table I, show a specific gravity difference of 0.2 between the bark and wood, the bark being 45 per cent heavier than the wood.

TABLE I

Specific Gravity of Hemlock Bark and Wood From Air-Dried Slabs

	Specific Gravity	Moisture Content (Wet Basis)
Wood	0.44	10.7
Bark	0.64	10.3
Knots	1.00	8.5

There is, therefore, a sufficient difference in specific gravity together with a difference in shape between the bark and wood to permit their segregation by this method. To make the difference in specific gravity and shape of the chips effective, the chips must be classified by size before air flotation.

The knots have a much higher specific gravity than the bark and since the knot shapes approach those of the bark rather than the wood, the knots can be expected to be discharged at the end of the separator deck with the heaviest bark fractions. This assures a knot-free wood product.

Process

For this study a one-half cord lot of hemlock slabs was procured from a sawmill in the Upper Peninsula of Michigan. The slabs which had been stacked to air dry for at least one year and stored under cover for two months were chipped and screened into five fractions. The coarsest fraction. consisting mostly of knots, was discarded; the finest fraction, consisting largely of bark was added directly to the bark product; and the other three fractions were each segregated separately by air floatation into a heavy fraction (bark), a light fraction (wood) and a middling fraction (bark and wood) and each middling fraction refloated. All heavy fractions were combined with the finest screen fraction to make up the bark product for tannin extraction and all light fractions were combined to form the wood product for pulping.

Chip Preparation: Air-dried slabs were used since limited qualitative tests made on several pulp-type gravity feed disk chippers showed that chipping of air-dried slabs resulted in the better detachment of bark and wood in the chips than chipping of green slabs. All slabs containing at least some attached bark were chipped in an experimental stationary model power-fed Carthage* disk chipper set to produce chips with a ¾" fiber length. The slabs containing

*The mention of commercial equipment does not imply that it is endorsed or recommended by the Department of Agriculture over other equipment of similar nature not mentioned.

no bark (about 10 per cent of the total) were not chipped in these tests, but in a production process they would be chipped separately and added to the wood fraction thus reducing the average cost of separation and slightly increasing the average purity of the wood chips. The chipper used has a 38″ diameter three-knife disk rotating in a plane about 30° with the horizontal. The horizontal feeding device consists of an upper and lower power-driven chain carriage which stabilizes the feed during chipping and aids in obtaining uniform chip lengths. In operation the slabs are fed in bark side up and the knives enter the bark side of the slab at an angle of 30° with the plane of the slab giving the bark a horizontal thrust which tends to detach the bark chip from the wood and cambium layers. Considerably better detachment of bark and wood was obtained than in a conventional gravity fed disk-type chipper.

A screen analysis of the chips together with a bark and wood analysis of each fraction is given in Table II.

TABLE II

Screen and Bark Analysis of Carthage–Chipped Air–Dried Hemlock Slabs
(10.5% Moisture on Wet Basis)

Screen Size	Retained on Opening	% of Total Wt. Retained	% Wood	% Bark	% Wood and Bark Adhering	% Wood in Adhering Portion	% Bark in Adhering Portion
Initial Material	——	100.0	63.8	36.2	1.0	53.3	46.7
+¾″	0.645″	31.6	72.8	27.1	2.2	31.2	68.8
—¾″ + 2–mesh	0.437″	32.1	69.4	30.5	1.0	30.2	69.8
—2–mesh + 3–mesh	0.279″	23.5	59.5	40.5	0.4	44.4	55.6
—3–mesh + 4–mesh	0.145″	3.3	44.0	55.9	0.1	——	——
—4–mesh + 7–mesh	0.094″	3.0	38.2	61.8	†	——	——
—7–mesh + 10–mesh	0.075″	1.6	37.6	62.4	†	——	——
—10–mesh + 20–mesh	0.0328″	1.0–	27.7	72.3	†	——	——
—20–mesh		3.9–					
		——	——	——	——		
		100.0	63.8‡	36.1‡	1.0‡		

† Insignificant amount
‡ Weighted totals

Complete detachment of the wood and bark occurred in 99 per cent of the total chips by weight. It is realized that this material may not be typical of what would be processed commercially. The long storage time undoubtedly favors detachment. Further studies are being made to determine the effect of such factors as the season of felling of the tree, seasoning of the slabs and the final moisture content upon the degree of detachment obtained during chipping.

Screening: Since the specific gravity differences are only moderate, close sizing of the feed material to the "specific gravity" separator is essential for

efficient segregation. For this purpose the chips were classified ona 2-deck Roball* gyrating screen into four main fractions—over ¾-inch, over 0.437-inch (2-mesh), over 0.279-inch (3-mesh) and through 0.279-inch. In addition a few large pieces estimated to be over 1½ inches were removed by hand since no suitable large screen was available.

*The mention of commercial equipment does not imply that it is endorsed or recommended by the Department of Agriculture over other equipment of similar nature not mentioned.

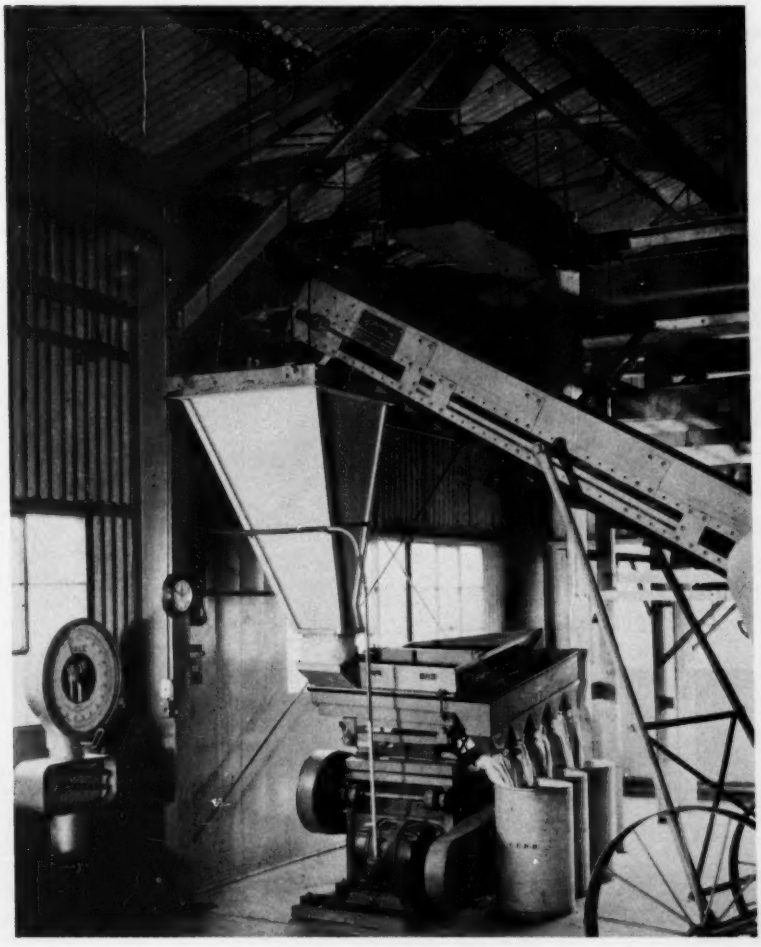

FIGURE 1.—Specific Gravity Air Classifier.

The bark-wood analysis of each screened fraction showed that the bark was more friable than the wood and thus the bark content increased with decrease in particle size. The fines through 0.279-inch, consisting of about 12.8 per cent of the total chips, contained about 64 per cent bark.

Segregation of Bark and Wood: The air flotation specific gravity separator used for this work was a Sutton, Steele and Steele model BX-100* shown in Figure 1. This equipment consists of an oscillating deck covered with a 16-mesh wire screen. Air supplied by a centrifugal fan is delivered through a system of baffles and through the porous covering to form a continuous upward air flow over the entire surface of the deck. The baffles are adjusted so that the maximum air rate is obtained at the rectangular section near the feed port (see Figure 2) with a slight gradual decrease in air velocity along the right deck rail to the so-called heavy end of the deck. There is also a uniform decrease in air velocity toward the light end of the deck where the lightest particles are discharged. The deck used in this work is fitted with tapering

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FIGURE 2.—Air Flotation Segregation of Hemlock Slab Chips.

riffles parallel to the deck discharge lip with decreasing height toward the heavy end of the deck. The volume of air delivered by the fan, the oscillating frequency of the deck, and the deck inclination are adjustable, the settings used being dependent upon the terminal velocity or floatability of the light fraction processed.

The feed is stratified into a light layer that floats off the deck surface and a heavy layer that rests on the surface. The light material floats over the riffle bars and migrates to the left or low end of the deck while the heavy pieces are propelled along the riffles toward the high righthand end by the oscillating motion. Material discharged over the deck lip falls into one of five chutes, in this discussion, numbered 1 to 5 from left to right (Figure 2). Adjustable baffles are provided to regulate the proportions of chips falling into each chute. As set up in Figure 2, only two baffles are in use to limit the middling fraction from chute 3. The wood products from chutes 1 and 2 are combined and the bark products from chutes 4 and 5 are combined.

Inspection of the chips showed that the wood was generally in the form of thin plates while the bark and knotty material were more like spheroids. These characteristic shapes tend to enhance the effect of specific gravity and aid their segregation in this equipment since spheroids are less influenced by the upward air flow than flat plates.

The three middle-sized chip fractions from the screening operation (over 0.75-inch, 0.437-inch, and 0.279-inch respectively) were each segregated into 5 fractions on this equipment. The middling fraction, from chute 3, was then refloated to give a finer segregation. In each case the middling fraction included about 25 per cent of the total feed. The flotations were all carried out at a feed rate of about 500 pounds per hour. Tests showed that substantially identical segregations can be obtained at about 1000 pounds per hour feed rate when the deck is fitted with a tail riffle on the lefthand end of the deck and a so-called dead skimmer baffle plate about 6 inches wide attached to the righthand rail.

No flotation separation was attempted on the small coarse fraction over 1½ inches, or upon the finest fraction, through 0.279 inch, since this would serve no practical purpose. The coarse fraction contained no bark and the material through 0.279 inch was too fine to be worth segregation.

Results and Discussion

A lot of 538 pounds of chips was screened and segregated using settings determined by small test runs. The results are shown in Tables III and IV and Figures 3 and 4. The quantities and compositions of the composite products listed in these tables are calculated in proportion to their occurrence in the main lot screened. The chips over 1½" consisted of a small fraction hand picked from the fraction over ¾ inch. They were mostly knots which are undesirable for either pulping or tannin extraction. This fraction should

TABLE III

Segregation of Bark and Wood from Hemlock Slab Chips by Air Flotation*

Chips Segregated				Wood Products				Middlings				Bark Products			
Screen Fraction				Chute 1		Chute 2		Chute 3		Chute 4		Chute 4		Chute 5	
Over, Inches	Through, Inches	% of * Total Chips	Bark Content %	% of* Total Chips	Bark Content %	% of* Total Chips	Bark Content %	% of* Total Chips	Bark Content %	% of* Total Chips	Bark Content %	% of* Total Chips	Bark Content %	% of* Total Chips	Barkt Conten %
0.75	1.5	31.4	25.4	10.61	0.2	5.19	0.7	7.44	18.1	——	——	2.04	79.2	6.12	81.2
0.437	0.75	32.1	29.9	8.53	0.1	6.23	0.9	8.51	22.1	——	——	4.91	86.6	3.92	86.8
0.279	0.437	23.5	33.9	8.88	0.7	3.34	4.5	4.49	36.7	——	——	2.56	88.2	4.23	91.0
Middlings Reflotation (Chips from Chute 3 above)															
0.75	1.5	7.44	18.1	1.35	0.8	1.87	1.8	1.61	5.5	1.79	35.6	——	——	0.82	70.6
0.437	0.75	8.51	22.1	2.4	0.9	1.9	1.8	3.0	27.3	——	——	0.3	72.6	0.9	88.4
0.279	0.437	4.49	36.7	0.55	3.1	0.62	6.5	2.16	29.2	——	——	0.53	74.2	0.63	89.7

* A total of 538 pounds of chips were processed including fines and material over 1½ inch not floated.

TABLE IV

Composite Products after Chip Segregation Calculated in the Ratio Produced

Fraction				Wood Products		Discards		Bark Products	
Over, Inches	Through, Inches	% of Total Chips	Bark Content, %	% of Total Chips	Bark Content, %	% of Total Chips	Bark Content, %	% of Total Chips	Bark Content, %
1½*	—	0.2	0	—	—	0.2	0	—	—
¾	1½	31.4	25.4	15.8	0.36	—	—	8.2	80.4
0.437	¾	32.1	29.9	14.8	0.44	—	—	8.8	86.7
0.279	0.437	23.5	33.9	12.2	1.7	—	—	6.8	90.1
—	0.279	12.8	64.1	—	—	—	—	12.8	64.1
				Middlings Refloated					
¾	1½	7.4	18.1	3.2	1.4	3.4	21.4	0.8	70.6
0.437	¾	8.5	22.1	4.3	1.3	3.0	27.3	1.2	83.4
0.279	0.437	4.5	36.7	1.2	4.9	2.2	29.2	1.2	82.6
Composite Products				51.5	0.96	8.8	24.9	39.7	78.2
Bark in Composite Product, % Total Bark				1.4		6.5		92.1	
Wood in Composite Product, % Total Wood				77		9.9		13.1**	

*Small fraction hand-picked from fractions over ¾ inch.

**Much of the wood chips in the bark product consists of knots which are undesirable for pulping.

be discarded. The fines through 0.279-inch contain too little wood of sufficient fiber length to be worth attempting to segregate for use in pulping. Since the bark content is high (64 per cent) in this fraction it can be added directly to the combined bark fractions for production of tanning material with little decrease in average tannin content or purity.

The chutes from the air deck are numbered from the light end, 1 and 2 producing wood fractions, 3 a "middling" fraction, and 4 and 5 predominantly bark fractions, except for chute 4 from reflotation of the middling fraction over ¾-inch which is also a middling fraction.

The separations obtained in this run gave practical products but an examination of Table III shows that absolutely ideal settings and results were not obtained. For example, the bark contents of the material entering the wood product from chute 2 during the flotation of the material over 0.279-inch and the reflotation of the middlings from the same material are excessive. Also, in the reflotation of the middling over 0.75-inch the bark content of the middling fraction from chute 3 is quite low. Slightly improved results could apparently have been obtained by small changes in the cutting finger locations for the middling fraction, particularly during the reflotation of the middlings.

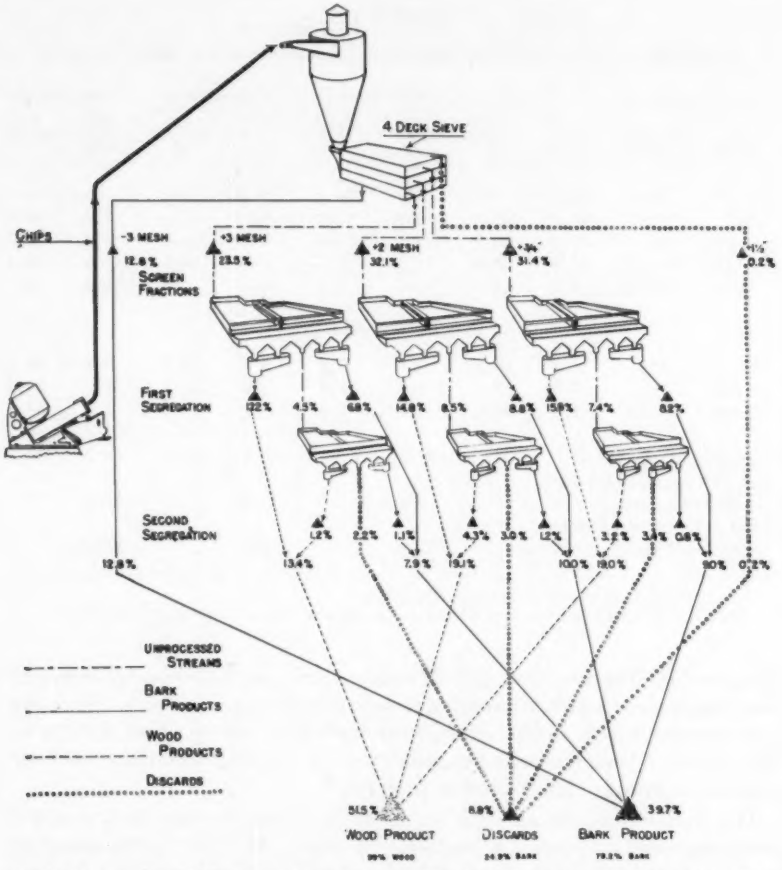

FIGURE 3.—Flow Diagram of Segregation of Wood and Bark from Hemlock Slab Chips.

Continuous recycling of the middlings back into the same flotation separator along with fresh material is not advocated here because the middlings consist of pieces of bark and wood with terminal velocities in the same range, and for this reason would be redischarged over the deck lip at the same location. Recylcing then, would tend to give less satisfactory separation of the wood and bark products. A more practical and better controlled segregation of the middlings can be obtained by refloating them separately. The middlings discarded from each screened fraction were reduced by about ½ or more by this method. Separate processing of the middlings permitted better control of the cuts. Precise settings of the cutting fingers on the initial segregation

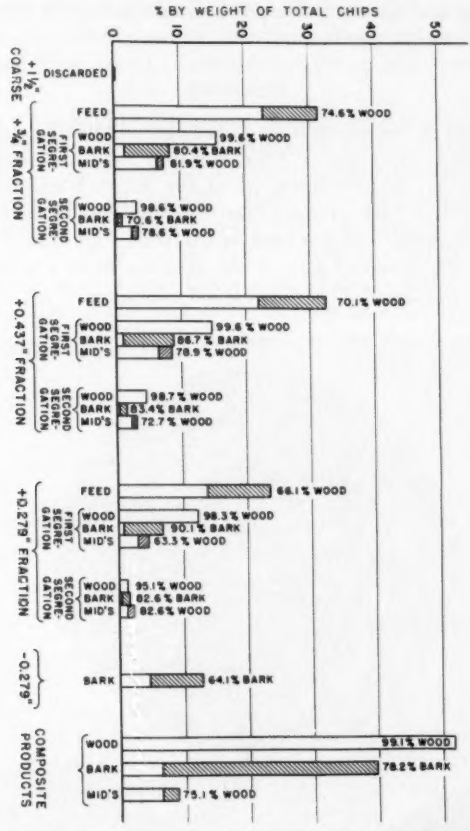

FIGURE 4.—Segregation of Bark and Wood from Air Dried Hemlock Slab Chips.

is difficult at high feed rates. A variation of ½-inch in the position of the cutting finger can materially change the bark content of the wood product. Conservative cuts may be made on the initial segregation when the middlings are processed separately. The middlings table can then be operated at lower feed rates and with more precise cuts since the middling material is now spread across the entire width of the table. A better separation of the middling fraction could be obtained by rescreening all middling fractions prior to reflotation since these fractions are generally made up of relatively small bark pieces or large wood pieces in addition to particles with adhering bark and wood. This step was not required to obtain good separations with the chips used here, however, and in a production process it is doubtful if additional

cost of screening and handling equipment could be justified by the increased yield of wood and bark products.

Products

A flow diagram of the segregation accomplished and the suggested recombination of various fractions to form suitable bark and wood products is shown in Figure 3. By combining all of the heavy fractions and the fines through 0.279-inch a bark product was recovered which contained 78.2 per cent bark and included 92.1 per cent of the total bark and 39.8 per cent of the total chips. By combining all of the light fractions a wood fraction was recovered which contained 99 per cent wood including 77 per cent of the total

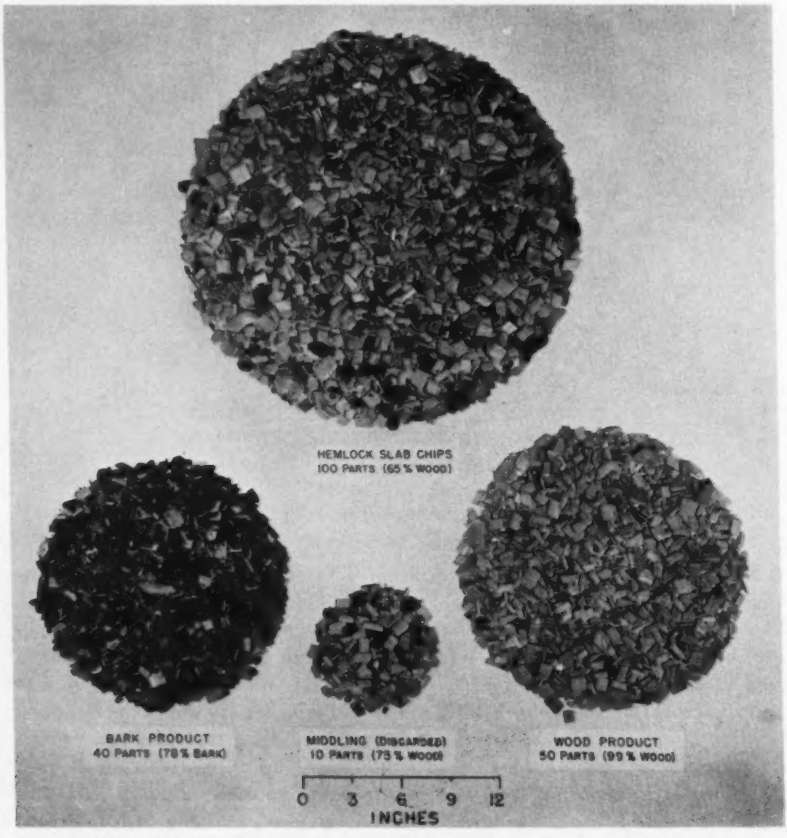

FIGURE 5.—Products Obtained by Air Flotation of Hemlock Slab Chips.

wood and 51.5 per cent of the total chips. Thus over 90 per cent of the slabs with attached bark can be converted into two valuable products and the slabs without attached bark would of course be 100 per cent used in the wood product.

Figure 5 is a photograph of the chips as received and products of the segregation process showing the relative proportion of the products obtained.

The bark product contained 10.3 per cent tannin on the dry basis. The tannin in this fraction had a purity of 66. This product should prove to be a good tannin raw material. Hemlock extract has long been used as a standard tanning material. Its properties are well known to tanners and thus should be readily marketable in the Great Lakes area. Table V gives the analysis of a representative sample of the bark product. The American Leather Chemists Association's standard method of analysis (8) was used.

TABLE V

Tannin Analysis of Bark Product

Soluble Solids, M. F. B.	15.59%
Soluble Nontannins, M. F. B.	5.26%
Tannin, M. F. B.	10.33%
Purity-basis of Soluble Solids	66.26%

The wood product, containing over 99 per cent wood should be an attractive source of pulp wood to paper and paperboard manufacturers who can tolerate a small amount of bark in their pulps. It would be highly satisfactory in all Kraft mills where hemlock fiber is used. The wood chips are quite uniform as to fiber length, free of hard knots and containing very little "dirt" or wood dust. These chips could be fed directly into digesters for pulping or mixed with the regular pulpwood chips at the paper mill.

Samples of pulp chips, containing 2 per cent bark, which were produced in an earlier air flotation experiment from chips containing an excessive fraction with attached bark and wood were submitted to several pulpmills for evaluation. This material was too high in bark content for use in sulfite mills producing quality paper but it was a satisfactory pulping material for a Kraft mill in the Upper Peninsula that was producing quality liner board.

The process described here can be altered to give different products if the market conditions and prices should warrant it. For example, if a wood product containing less bark could sell at a sufficient premium it would be possible by combining the proper fractions to produce a product containing 99.7 per cent wood consisting of 28 per cent of the total chips together with one containing 98.3 per cent wood and consisting of 23.5 per cent of the total chips. On the other hand, by adjusting the cuts on the middlings table the auxiliary wood product could be increased and made to meet a specification

of 95 per cent wood. This would result in a discard portion of only about 5 per cent including the 1½ inches overs. Furthermore, if such markets are not available and it is desirable to produce a 95 per cent wood product only, as would be likely if paperboard manufacturers are to be supplied, then by combining all of the middling portions a wood product containing 95.6 per cent wood and consisting of about 60 per cent of the total slabs could be produced. The plus 1½ inch knots would then be the only portion discarded or used for fuel. These variations would not change the bark product.

Preliminary cost estimates indicate that the process will be of commercial interest if the separation of bark and wood obtained in these chipping and segregation tests could be obtained commercially. At the present time work on the effect of moisture content and age of the slabs as well as the felling period of the logs on the chipping and subsequent segregation is being investigated so that definite recommendations as to the condition of the raw material can be made.

As suggested by the work of Calderwood and May[2] and by Snow[4] the possibility of segregating bark and wood from chipped round wood such as tree tops and limbs should be investigated. Use of such material could prove very valuable in reducing logging residues. In-the-woods-chipping would be involved and seasoning of the round wood may be required with the added problem of transporting chips from the logging area to the processing plant. It is probable that detachment of bark and wood during the chipping of round wood would be reduced with consequent loss of efficiency in the segregation of the bark and wood.

Summary

A large volume of hemlock slabs and edgings is largely wasted each year at sawmills in the Upper Peninsula of Michigan. The segregation and recovery of hemlock bark from these slabs for use as a tanning material source is considered here. A test lot of year-old air-dried hemlock slabs was chipped in a power-fed disk-type chipper. The chips were then size classified by screening into 5 fractions. The coarsest fraction. which contained largely knots, was discarded. The three middle fractions were each segregated on an air flotation specific gravity separator to produce a wood product, a bark product and a middling fraction. The middling fractions were then refloated to give additional wood and bark products. The bark fractions blended together with the finest screened fraction which was not air floated gave a combined bark product which contained over 10 per cent tannin and included about 92 per cent of the total bark in the slabs. The combined wood product contained 99 per cent wood and included 77 per cent of the total wood in the slabs.

The process could be adjusted to produce wood chips with somewhat less bark but with a lower yield, or if more bark could be tolerated in the wood chips a higher yield could be obtained.

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Stratigraphic Distribution Studies of Salt Penetration into Hides

By C. C. KRITZINGER and J. H. M. VAN ZYL

In an early study McLaughlin and Theis [2] investigated the distribution of salt in hide cured for varying periods by the application of solid salt, but they had no means of obtaining accurate splitting of the hide into more than three layers. Such a method became available when Kritzinger and Theis [1] developed a technique for splitting leather into a number of layers, of equal thickness through the use of a freezing microtome, and it has been used by Strandine, deBeukelaer and Werner [3] to follow the penetration of salt into hides brined under different conditions of experimentation. Stubbings [4] has used the same technique for studying the distribution of salt in calfskin cured for two up to ninety days with solid salt, but there is still no knowledge of the distribution picture during the actual penetration of the salt, i. e. during the first 24 hours. For this reason the present study was undertaken.

Experimental Methods

Square samples of hide from the butt area were given about 50 per cent by weight of good quality salt, and inserted amongst hides which had already been in a salted stack for a period of four days, in order to simulate practical conditions and to avoid unnecessary loss of moisture through evaporation. Discs of about one inch in diameter were taken from these samples after 2, 6, 12, 18, 24 and 48 hours and immediately sliced into ten layers of equal thickness on a freezing microtome. We found it necessary to cover the discs on the freezing stage with a small beaker, to avoid undue uptake of moisture from the air while freezing was in progress. The slices were covered immediately with a sheet of glass to avoid loss of moisture before sampling and weighing for the different determinations. Cutting and weighing operations were usually completed within half an hour after taking the sample discs from the salted squares.

Expression of Results

Strandine, deBeukelaer and Werner recorded their results as percentage of the cured hide as is, and only calculated the degree of saturation of the residual moisture by the salt taken up. While this method has several advantages in certain cases, we found it better in our work to express salt taken up either as a percentage by weight on the residual moisture or as a percentage by weight on the hide substance. Likewise we have expressed moisture as percentage by weight on hide substance. With this method we can get a clearer picture as to why the salt moves in a definite pattern, but it must be admitted that the method has certain limitations. For example, due to the high fat content in say the flesh layers, the hide substance will be relatively

TABLE I

The Stratigraphic Distribution of Sodium Chloride (as % by Weight on Water) in Hide Cured for Varying Periods with Solid Salt.

Layer (Grain)	Hours of Curing						
	0	2	6	12	18	24	48
1	1.95	3.4	5.8	14.5	19.1	26.3	33.7
2	2.01	3.3	5.7	15.2	19.4	24.8	33.9
3	2.04	3.9	6.3	15.5	19.9	24.2	30.4
4	2.14	4.9	7.2	15.9	20.3	24.5	29.0
5	1.69	6.3	9.4	16.6	20.7	24.6	29.5
6	1.69	8.1	11.6	18.1	22.2	25.3	32.2
7	2.04	10.6	15.1	21.0	24.5	27.3	33.5
8	2.05	14.4	17.9	23.1	26.7	28.4	33.0
9	1.87	18.3	20.4	25.6	28.0	29.1	31.0
10 (Flesh)	1.82	19.6	21.8	26.6	28.9	29.5	31.8

TABLE II

The Stratigraphic Distribution of Sodium Chloride (as % by Weight on Hide Substance) in Hide Cured for Varying Periods with Solid Salt.

Layer (Grain)	Hours of Curing						
	0	2	6	12	18	24	48
1	5.29	9.1	13.0	22.2	26.4	31.3	33.7
2	5.94	7.9	10.9	18.0	21.8	26.8	32.2
3	3.99	7.1	8.9	16.1	19.2	22.3	27.8
4	3.25	7.3	9.2	15.5	18.1	20.3	26.1
5	2.42	8.4	11.5	15.8	17.9	19.9	26.4
6	2.34	10.2	13.5	17.6	20.4	21.0	28.6
7	2.69	12.3	16.4	21.2	24.2	24.1	30.5
8	2.83	14.4	20.0	25.9	29.4	30.0	33.9
9	2.94	20.9	28.8	35.4	37.5	38.4	38.7
10 (Flesh)	2.93	35.5	44.3	50.3	50.2	50.2	50.5

TABLE III

The Stratigraphic Distribution of Water (as % by Weight on Hide Substance) in Hide Cured for Varying Periods with Solid Salt.

Layer (Grain)	Hours of Curing						
	0	2	6	12	18	24	48
1	271	263	224	153	138	115	100
2	295	241	191	118	112	108	95
3	195	183	142	104	96	92	91
4	151	147	127	98	89	83	90
5	143	132	123	95	87	81	89
6	138	126	116	97	92	83	89
7	132	115	109	101	99	88	91
8	138	100	112	112	110	106	103
9	157	114	141	138	134	127	128
10 (Flesh)	161	182	203	189	174	170	159

lower, hence the water expressed on hide substance will be rather high, whilst actually a portion of that water is derived from between the fat deposits. Nevertheless we think that we obtain a clearer picture of the position, as shown in Tables I, II and III and Figures 1, 2 and 3.

Discussion of Results

The values recorded in Tables I, II and III have been plotted in Figures 1, 2 and 3. The state of the hide will be discussed at each period of sampling.

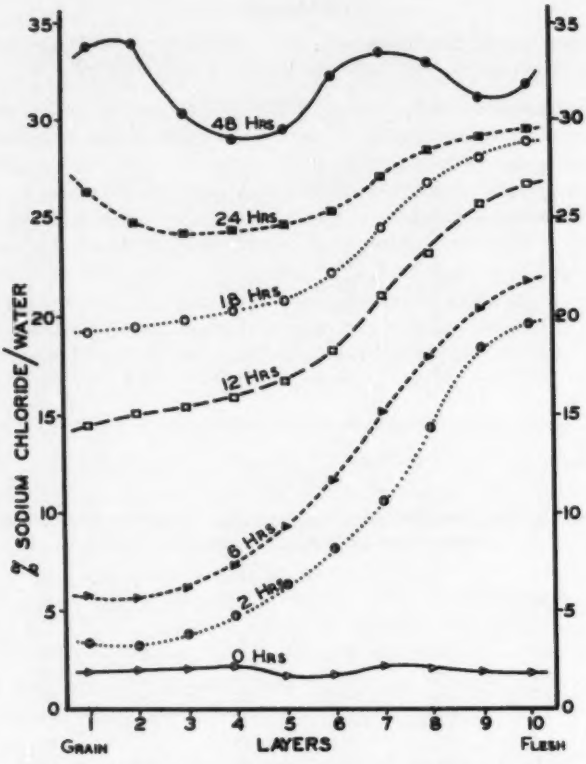

FIGURE 1.—The Stratigraphic Distribution of Sodium Chloride (as % by Weight on Water) in Hide Cured for Varying Periods with Solid Salt.

Fresh Hide

The moisture content of the fresh hide shows considerable variation throughout the ten layers taken, being very high in the region of the active organs of the epidermal region and low in the central layers. Near the flesh side (layers 9 and 10) there is a slight increase. Note that the moisture content, calculated on hide substance is twice as high in the epidermal region as in the central corium layers. When calculated as moisture on the hide as is, the difference is not as much. This is due to the relatively larger free spaces (glands etc.) in the epidermal region, spaces which will naturally contain more water, and to the higher fat content of this region over the corium proper. The moisture curve obtained by this method of calculation is identical to that obtained by calculating moisture on the hide as is. (See Strandine, deBeukelaer and Werner, Fig. 1.)

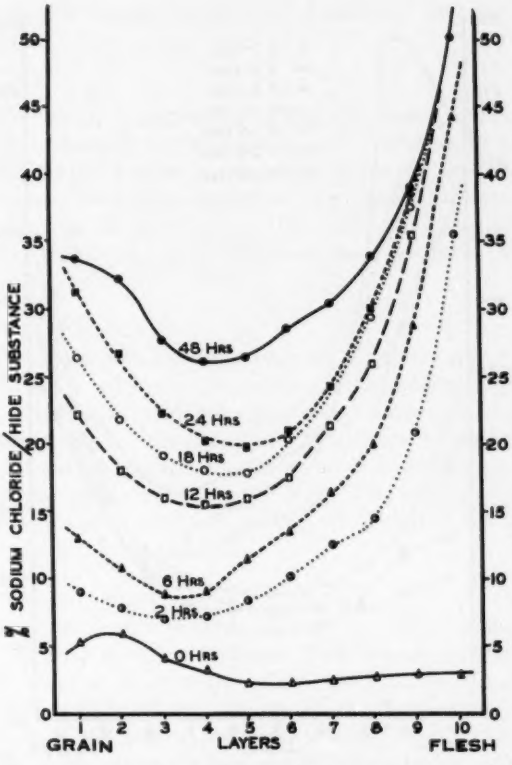

FIGURE 2.—The Stratigraphic Distribution of Sodium Chloride (as % by Weight on Hide Substance) in Hide Cured for Varying Periods with Solid Salt.

Whereas the salt content of the hide (based on hide substance) is somewhat higher in the epidermal region the concentration of the salt solution in the moisture present shows only small variations, being slightly lower in the centre of the corium. Once again these results fully confirm those of Strandine et al.

Two Hours' Curing

After two hours of curing the salt concentration has increased throughout the entire hide, but very much more so in the layers towards the flesh side. The amount of salt present (based on hide substance) follows the same trends as the salt concentration (based on moisture), but there is already a tendency for the two layers nearest the grain surface to show more salt. This is merely due to the fact that the salt concentration shows a downward

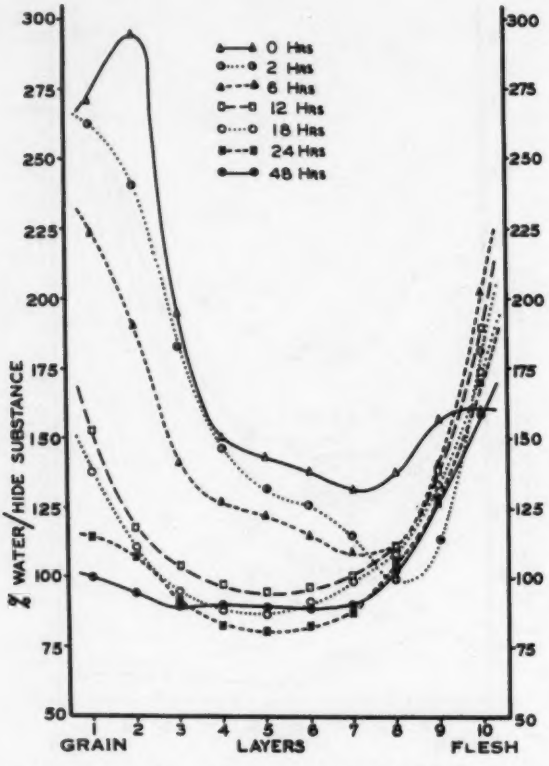

FIGURE 3.—The Stratigraphic Distribution of Water (as % by Weight on Hide Substance) in Hide Cured for Varying Periods with Solid Salt.

gradient, which would force salt movement in this direction. It is also clear that while the salt moves into the hide, water is moving outwards towards the flesh. The hide pieces had been in contact with salt on the hair side as well, but quite obviously there is at this stage no sign of salt moving into the hide from the grain side. A small loss of moisture might, however, have taken place through the grain side, although it is doubtful at this stage.

Six Hours' Curing

The salt concentration has again increased through the entire hide, the amount of salt still showing the trends present after two hours. Note that the increase is very uniform for all the layers, both for concentration and for total amount present. The water has decreased further in the layers nearer the grain, but seems to have collected in the two flesh layers. The salted hide at

this stage is roughly comparable to a hide brined for four hours (see Strandine et al, Fig. 2).

Twelve Hours' Curing

There is a relatively larger change during the second six hour period than during the first, especially in the layers from the centre to the grain. The salt concentration and the amount of salt present show this increase very clearly. Note that the salt concentration gradient is still such that movement of salt must take place in the direction of the grain. The water has decreased rapidly in the epidermal region, but there has been little change near the flesh side.

Eighteen Hours' Curing

During the period from twelve to eighteen hours the water shows a fairly uniform decrease in all the layers, although the tendency is still to collect on the flesh. The salt concentration now shows a more rapid increase in the layers from the centre to the grain, but there is still no sign of salt entering in quantities from the grain side, hence the concentration gradient is such that salt still moves inwards from the flesh. This is shown quite clearly by the curve from the amount of salt present. Note that in the two flesh layers the amount of salt has not increased.

Twenty-four Hours' Curing

The water shows a uniform decrease in all the layers, except the first grain side layer where the decrease is larger. This is quite probably due to relatively quicker loss of moisture through evaporation at this stage. The salt concentration has built up only slightly on the flesh side, but in the layers from the centre to the grain the increase is large. Now for the first time the concentration in the first and second grain layers is higher than in the central layers, which would stop further movement from the flesh side. This may be due either to salt entering from the grain side, or to loss of moisture through evaporation on this side or to both factors at the same time. The amount of salt present is high in the epidermal region, low in the centre and has not changed on the flesh side. The overall picture is similar to that of a hide brined for 24 hours, as depicted by Strandine et al in their Fig. 3.

Forty-eight Hours' Curing

There has been very little change in the distribution or in the amount of water present. The central layers appear to have taken moisture from both the grain and the flesh sides, being slightly higher than at 24 hours. The amount of salt present has increased only slightly on the grain side, not at all on the flesh side and quite considerably in the central layers, but is still low in this area. The salt concentration curve shows very interesting features. It is quite high in the two grain layers, and since there has not been such a

rapid change in the moisture content of these layers, it indicates that salt is now also moving in through the grain. The concentration is above saturation point, however, hence some evaporation must have taken place. The layers from the centre to the flesh also show a much higher concentration, again slightly above saturation point, whilst layers 9 and 10 on the flesh have more or less reached saturation. The salt concentration curve is similar to that in a hide brined for four days (see Strandine et al, Fig. 4). Unfortunately the work had been discontinued at this stage so that it was not possible to follow further changes. It would seem to stand to reason that the concentration curve will become somewhat more uniform, especially in layers 3, 4 and 5 which have not reached saturation. This is also indicated by the results obtained by Strandine et al. However, due to evaporation losses it is doubtful whether an entirely uniform curve will be achieved even after several weeks.

Summary

1. In a fresh hide the layers of the epidermal region contain more water than the corium layers. The amount of salt is also somewhat higher, but the concentration of salt is very nearly uniform throughout the hide.

2. When solid salt is applied to a fresh hide, some of the salt will form brine in the surface moisture and will penetrate rapidly from the flesh side. This causes a movement of water from the grain to the flesh layers, so that in a hide cured for 48 hours there is less water in the grain layers than in the flesh layers.

3. Although there is a loss of water through evaporation on the grain side, salt does not penetrate from this side in any appreciable quantities during the first 24 hours of curing.

4. Although the overall analysis of a hide cured for 48 hours shows saturation of the residual moisture with salt, the concentration of salt in the layers varies somewhat at this stage, some of the central layers nearer the grain side having a concentration below saturation point. Prolonged curing will probably result in saturation of all the layers, but those layers near the grain and flesh sides will then have more salt present than could be in solution in the residual moisture.

Leather Industries Research Institute,
Grahamstown, South Africa.
26th March, 1953.

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A Study of the Spoilage of Stored Wet-Salted Hides Cured for Varying Periods

By C. C. KRITZINGER

INTRODUCTION

Almost all of the past investigations on the curing of wet-salted hides, as summarized by Hausam,[6] have been concerned with the rate of putrefaction during curing and during subsequent storage. In general it has been found that the longer the curing period the more pronounced is the breakdown of the proteins. This is to be expected, in view of the findings of Anderson[1] that bacteria readily develop salt-resistance and will therefore assist natural halophylic bacteria in attacking the hide proteins. The practical demonstration of protein breakdown is hairslip. It has been shown that bacteria first attack the readily available and more labile globular proteins[4, 5] which cement the epidermis and hair to the underlying tissues, and when these proteins have been affected sufficiently hairslip must occur[10].

Despite the knowledge that prolonged curing must inevitably result in more pronounced putrefaction, unless antiseptics are used in the process, no study has been made of the influence of the length of the curing period upon the rate of putrefaction or, as a corollary, of the minimum period of laying away in salt required by the hides. Stather and Herfeld[15], recently confirmed at this Institute by van Zyl[20], have shown that the residual moisture in the hide can be saturated within 24 hours under ideal conditions, while Stuart and Frey[16] proved that putrefaction would occur more rapidly if this moisture is not saturated with salt. This work was confirmed recently on large scale by Kritzinger[11], who showed that more putrefaction occurred the longer the hides were kept in stack, even when 100 per cent salt on hide weight was applied. Bacterial attack was, however, much faster and more pronounced when too little salt (25 per cent on hide weight) was used. Under the latter conditions the residual hide moisture could not be saturated.

It would therefore appear that the prime factor in determining the efficiency of curing of wet-salted hides is saturation of the water retained by the hide, and since this can be achieved within at least three days under practical conditions, there seems to be no reason for keeping hides in stack for periods up to a month as is regular practice at present. In South Africa the curing period was decreased to ten days during the war with apparently no ill effect upon the inherent quality of the goods. An American firm[2] has adopted a method whereby the hides are brined in a solution kept saturated with salt for a period of about 24 hours, and finds that the hides are perfectly preserved by this treatment, requiring no further salting. Many tanners, however, maintain that hides which have been in salt for less than the accepted 30 days will be in greater danger of putrefaction when subsequently stored in

the tannery without the addition of salt as is regular practice in certain countries.

Experimental Procedure

Using approximately 60 per cent good quality salt on hide weight, well washed summer hides were cured for 30, 10, 7, 5, and 3 days in single stacks, with 110 hides in each stack. One series was run as control and a second with salt containing 2 per cent sodium silicofluoride. The different stacks were built in such a manner that all were opened on the same day at the end of the specified curing period.

After curing, the salt was shaken off, a sample cut on the bend near the backbone and about 12 inches from the tailroot from 30 hides in the center of each stack, and the hides bundled and weighed to determine the shrinkage (weight loss) during curing.

After one week, which was taken as being the equivalent of transit, the bundles were opened, the salt shaken off again and weighed, the same 30 hides in each lot sampled again and the hides then weighed to determine "transit loss". The hides were now re-stacked *without salt* in the manner practised by tanners. After a further two weeks the same hides were again sampled, the salt shaken off and weighed and the hides weighed. Once more the hides were re-stacked for four weeks and the procedure repeated. The hides had therefore been in store without salt for a period of seven weeks after curing.

The hides were now bundled and moved to a tannery where the received weight was recorded and the stock then soaked and limed. After liming, the goods were allowed to drain for one hour and were then weighed to determine the limed yield, the fleshing operation being omitted. In previous studies[11] it was found that fleshing confused the picture too much.

The samples taken from the hides were analyzed by methods previously described[9] for moisture, sodium chloride, nitrogen extractable by water during three hours' milling at 60 r.p.m. and volatile nitrogen. In Table I the concentration of sodium chloride in the residual moisture is shown and the nitrogen figures represent percentages of the total hide nitrogen.

Examination of the Hides

When the stacks were opened at the end of the curing period the following observations were made.

1. The hides were progressively drier the longer the curing period.

2. The five lots treated with sodium silicofluoride in the salt were wetter than their corresponding controls. Robertson[13] had found that such hides appeared drier in her experiments.

3. Red heat had developed only on the 30-day control lot and a slight putrid smell was perceptible. All the other hides were free from red heat and had a clean "sweet" smell.

4. Six of the ten lots were very clean but the remaining four (the 3- and 7-day control as well as silicofluoride batches) were somewhat dirty owing to inefficient washing.

5. In all cases except the 30-day lots the silicofluoride hides appeared slightly dirtier and especially redder than their corresponding controls. This seems to be due to some unknown action of silicofluoride whereby the blood appears to be left on the surface. In fact, but for the absence of the typical slimy feel, the hides had the appearance of stock slightly attacked by red heat. When curing is prolonged to about three weeks, the red colour disappears again, leaving the hides whiter than the controls.

During subsequent storage over a period of seven weeks the following changes occurred in the hides.

1. Drying took place progressively, but more notably so along the exposed edges. The centre portions stayed quite wet.

2. Despite such drying the differences in degree of wetness present after curing seemed to persist.

3. Red heat developed after about three weeks in all the control hides, but was more pronounced on the 30-day group. The silicofluoride hides did not even develop localized spots of red heat, mixing having been done very thoroughly[9]. The degree of red heat development in the control lots was much less than that which is normally present during such a period when excess salt is used. The experimental hides had been shaken free of all salt and under such conditions red heat does not develop readily[11] or at least does not show up so clearly on the flesh side.

4. The control hides now exhibited a progressively stronger putrid smell, but all the silicofluoride hides had a fresh "sweet" appearance and handle. At the end of storage the silicofluoride hides were also much cleaner than their corresponding controls.

The over-all impression was that all the hides had been well cured although no special effort was made to obtain a perfect cure. It also seemed that the hides which had been in cure for 30 days had deteriorated more during storage than the 3-day hides where no silicofluoride was present.

The tanner had been given no information regarding the curing processes used on the various lots and reported as follows: "Although we examined the quality of all hides as delivered in their various groups very carefully, we found no traces of 'red heat' or putrefaction either in the form of hair-slip or bad odours, and we are quite unable to state that any particular parcel was superior to any of the others. The quality of the stock after liming was indeed a revelation to us, and they were undoubtedly the finest hides we have seen in this tannery from a point of view of cure, for some considerable time. Here again we found it impossible to distinguish one pack from the other and found no traces of putrefaction whatsoever, the pelt being in ideal condition.

TABLE I

Changes in Stored Wet-Salted Hides Cured for Varying Periods with and without Sodium Silicofluoride

TREATMENT	CONTROL TREATMENT					2% SODIUM SILICOFLUORIDE ADDED TO SALT				
DAYS CURING	3	5	7	10	30	3	5	7	10	30
Green weight (lb)	6,830	6,935	7,480	6,697	6,947	7,600	6,887	8,080	7,375	7,395
Cured weight (lb)	5,735	5,686	6,060	5,380	5,452	6,535	5,802	6,735	6,120	6,039
% *Shrinkage*	16.0	18.1	19.0	19.6	21.5	14.0	15.8	16.7	17.0	18.3
Weight after one week storage (lb)	5,543	5,534	5,923	5,237	5,275	6,275	5,622	6,485	5,878	5,791
% *"Transit loss"*	3.3	2.7	2.3	2.7	3.3	4.0	3.1	3.7	3.9	4.1
% Total shrinkage	18.8	20.2	20.8	21.8	24.1	17.4	18.4	19.7	20.3	21.7
Weight salt shaken off (lb)	73	78	65	75	85	80	75	72	78	85
% Salt (on cured weight)	1.3	1.4	1.1	1.4	1.6	1.2	1.3	1.1	1.3	1.4
Weight after three weeks' storage (lb)	5,490	5,470	5,863	5,200	5,226	6,220	5,568	6,405	5,829	5,755
% Total shrinkage	19.7	21.1	21.6	22.4	24.8	18.2	19.2	20.7	21.0	22.2
Weight salt shaken off (lb)	16	12	20	12	16	16	15	18	20	15
Weight after seven weeks' storage (lb)	5,429	5,438	5,818	5,148	5,173	6,108	5,482	6,348	5,767	5,686
% Total storage loss	5.3	4.2	4.0	4.3	5.1	6.5	5.5	5.8	5.8	5.9
% Total shrinkage	20.5	21.6	22.2	23.2	25.6	19.2	20.4	21.5	21.8	23.1
Weight salt shaken off (lb)	9	12	12	12	6	10	10	14	10	8
Total weight salt shaken off (lb)	98	102	97	99	107	106	100	104	108	108
% Salt (on cured weight)	1.7	1.8	1.6	1.8	2.0	1.6	1.8	1.6	1.8	1.8
Total tannery received weight (lb)	5,305	5,332	5,729	5,106	5,121	5,970	5,315	——	5,704	5,573
% Transit loss	2.3	2.0	1.5	0.8	1.0	2.3	3.0	——	1.1	2.0
Limed yield on green weight (%)	128.9	127.4	127.9	127.2	128.6	129.8	128.9	——	129.0	129.3
Limed yield on cured weight (%)	153.5	155.4	157.9	158.4	163.8	151.0	153.0	——	155.5	158.4
% *NaCl on Moisture*										
After curing	32.5	32.3	32.2	32.7	33.1	32.4	32.2	32.5	32.5	32.9
After one week's storage	32.7	32.3	32.6	32.7	33.3	32.8	32.4	32.6	32.6	33.0
After three weeks' storage	33.1	32.9	33.1	32.6	33.6	33.0	32.7	32.9	33.0	32.7
After seven weeks' storage	32.9	33.2	33.0	32.8	33.4	33.3	32.9	33.2	32.9	33.2
% *Extractable Nitrogen*										
After curing	1.92	2.00	2.09	2.17	2.43	1.91	1.95	2.01	2.08	2.20
After one week's storage	2.07	2.20	2.28	2.40	2.63	1.96	2.04	2.13	2.25	2.34
After three weeks' storage	2.39	2.45	2.55	2.67	2.81	2.14	2.18	2.28	2.37	2.52
After seven weeks' storage	2.60	2.71	2.80	2.93	3.06	2.30	2.33	2.37	2.49	2.65
% *Volatile Nitrogen*										
After curing	0.16	0.17	0.17	0.18	0.25	0.12	0.13	0.14	0.13	0.13
After one week's storage	0.18	0.19	0.20	0.21	0.30	0.13	0.13	0.15	0.14	0.14
After three weeks' storage	0.21	0.23	0.25	0.28	0.39	0.15	0.15	0.16	0.16	0.16
After seven weeks' storage	0.28	0.32	0.36	0.41	0.58	0.16	0.16	0.17	0.17	0.17

We were naturally interested in the finished product and examined the leather carefully after tanning. We could detect no ill effects from the use of sodium silicofluoride in the cure. Some of the hides were processed for harness, some for sole and insole leathers and a few for chrome, but they were all quite satisfactory on completion of tanning."

All factual information is given in Table I.

Shrinkage During Curing

Since the loss of water from a fresh hide is always greater than the amount of salt taken up during wet-salting or brining, there is a loss of weight from the green to the cured condition known as shrinkage., expressed as a percentage weight loss on the green weight. Under a given set of conditions this shrinkage is directly proportional to the length of the curing period as shown in Table I and Fig. I, the loss being greater the longer the curing period lasts. From these results and those reported earlier [11] it is obvious that the rate of weight loss is fast during the early stages of curing but tends towards

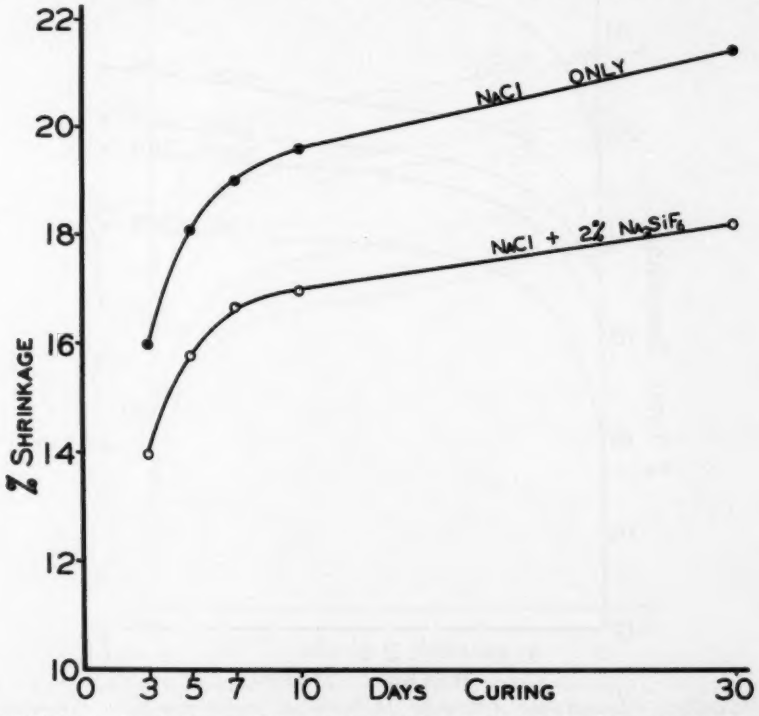

FIGURE 1.—The Influence of Time on the Shrinkage During Curing of Wet-salted Hides.

some maximum around 30 days. Perhaps it is for this reason that tanners consider 30 days as the minimum curing period, especially where hides are bought on the cured weight basis.

It is important to note that, despite the wide variations (14 .0 per cent to 21.5 per cent) in the shrinkage values for the two series, the residual moisture in the hides in all cases is saturated with sodium chloride and that there is very little difference between the various groups. See Table I. This can only mean that the end of curing, with respect to the concentration of salt in the residual moisture is reached within three days. Any further increase in the curing shrinkage must then be due to running off of saturated brine and not to a gradual evaporation of moisture. In the latter case there would have been a steady increase in the ratio between salt and moisture, i. e.

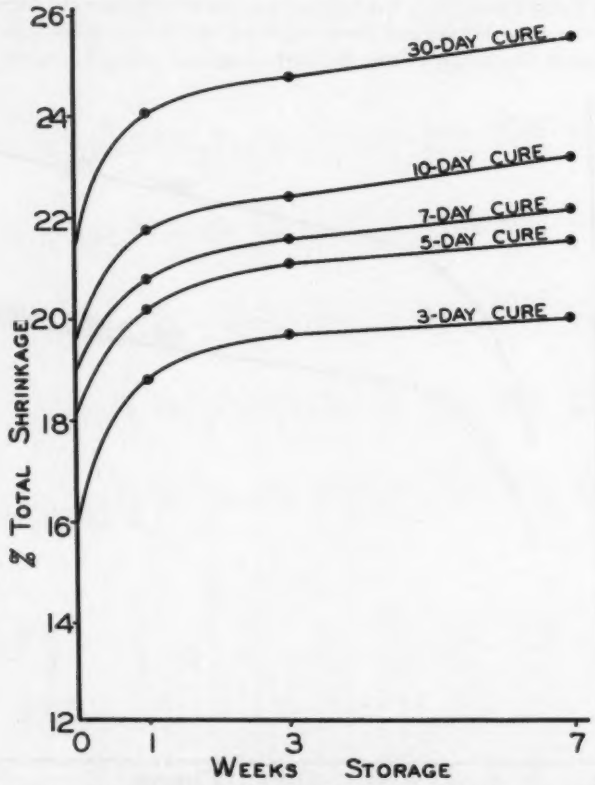

FIGURE 2.—The Influence of Time on the Shrinkage, During Storage, of Wet-salted Hides Cured for Varying Periods with Salt Only.

some salt would have to crystallize out. This has obviously not happened in the hides under consideration.

The addition of 2 per cent sodium silicofluoride to the curing salt has again resulted in a decrease in the shrinkage as reported earlier in Australia [8] and by Kritzinger [9, 11, 12], the shrinkage being from 2 to 3 per cent lower than for the controls. It is interesting to note that the difference in the shrinkage figures for the two series increases slightly with time.

Shrinkage and Salt Loss During Storage

Figs. II and III show the increase in the total weight loss (curing plus storage) during seven weeks' storage of hides cured with and without sodium

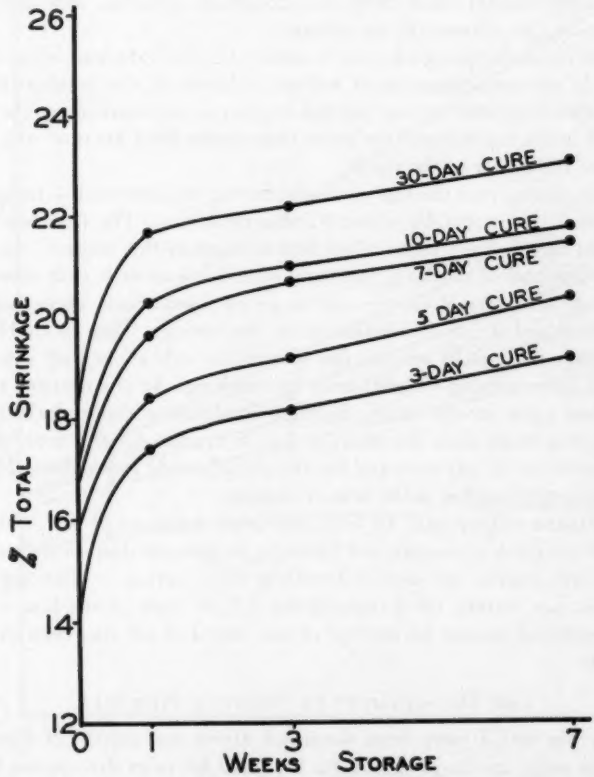

FIGURE 3.—The Influence of Time on the Shrinkage, During Storage, of Wet-salted Hides Cured for Varying Periods with Salt Containing 2% Sodium Silicofluoride.

silicofluoride added to the salt. The values shown at 0 weeks' storage are those of the shrinkage at the end of curing as depicted in Fig. 1.

These graphs show the expected logarithmic curve, i. e. loss in weight during storage is relatively faster during the initial period and tends towards a maximum after seven weeks. At this stage, however, the difference in shrinkage between the various lots still maintains. The first week is the equivalent of transportation and in view of the logarithmic nature of the drying out curve it is to be expected that big losses in weight can occur between the curer and the tanner. It is, however, important to note that despite the wide variations in the length of the curing period and the degree of wetness of the stock, the weight loss during the first week (Per cent "Transit Loss" in Table I) is quite constant for each series, with the silicofluoride hides losing slightly more weight than their corresponding controls, and also slightly more during the subsequent six weeks.

Some of this loss through drying is reflected in the values showing the slight increase in the concentration of sodium chloride in the residual moisture, but it is also clear that drying had taken place much more along the exposed edges and in the top hides of the stack than in the bend areas of the sampled hides from the center of the stack.

It might appear that the loss in weight during the first week ("transit loss") is more than that normally allowed in South Africa. The franchise is 2 per cent. Two factors have to be taken into account in this respect. In the first place the method of stacking the bundled hides was such that more drying would occur than would be the case in an enclosed truck, except under the very hottest and driest of conditions on the railway. The second factor is the fact that the loss in weight also reflects the salt shaken off (an average of 1.3 per cent on cured weight) prior to weighing. In the tannery the hides are weighed upon receipt in the bundled condition without shaking off the salt. On this basis then the average loss in transit for the controls would have been about 1.5 per cent and for the silicofluoride hides about 2 per cent if they had been handled in the normal manner.

It is of practical interest to note the large amounts of salt which were shaken off the hides as storage and handling progressed, despite the care taken to shake free excess salt before bundling after curing. After one week's storage the salt shaken off accounted for 1.3 per cent of the loss in weight and at the end of storage an average of one pound of salt had been shaken off every hide.

The Development of Volatile Nitrogen

The factors which have been discussed above are mostly of commercial importance only, insofar as they form the basis for price discussions between the curer and the tanner where hides are bought on the cured weight basis. These factors do not necessarily reflect upon the true inherent quality of the goods.

The quality of the hides was assessed by a purely relative judgment based on their appearance, handle and smell as described above. From this it would seem that there is a slight difference in favour of the hides receiving the shorter cure. Two further criteria were used to ascertain the quality of the raw stock before reaching the tannery. Since bacterial attack on proteins results in the formation of readily soluble and volatile nitrogenous breakdown products, a determination of such nitrogen gives a measure of the efficiency of the cure and of the rate of putrefaction during storage. This method of quality assessment has been developed during the past twelve years by Koppenhoefer

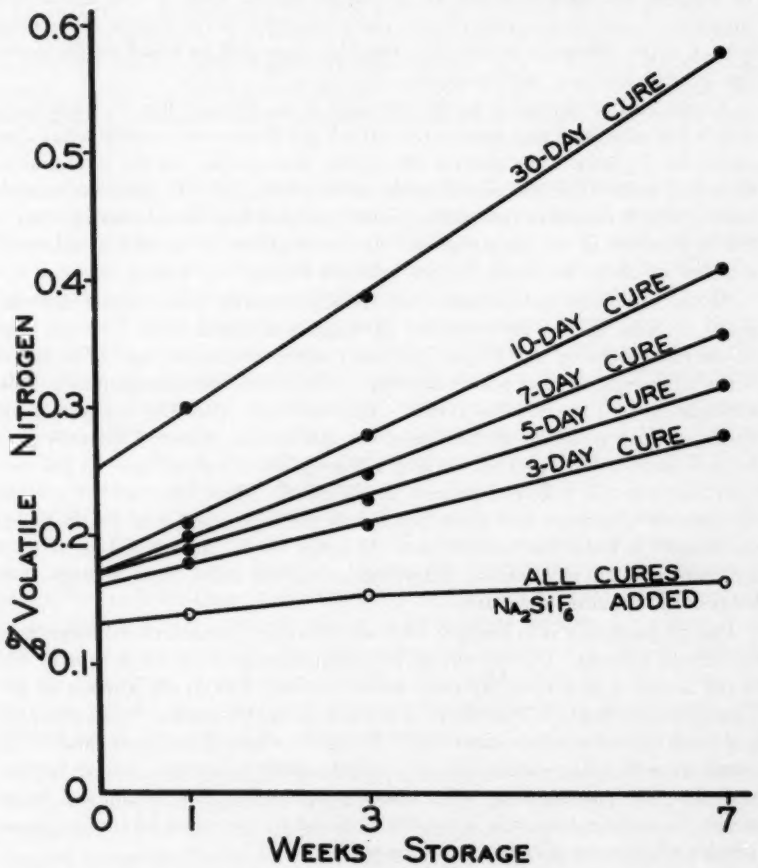

FIGURE 4—The Development of Volatile Nitrogen During Storage in Wet-salted Hides Cured for Varying Periods with and without Sodium Silicofluoride.

and Somer[7], Somer[14], Stuart and Frey[17, 18, 19], Kritzinger[8, 9, 11] and Whitmore and co-workers[21, 22].

Table I shows the amount of nitrogen extractable with water during three hours milling at 60 r.p.m. The value increases with the length of the curing period as well as the storage period, indicating progressive breakdown of proteins. It is possible that part of this breakdown is due to the action of the salt itself, as indicated by the fact that this increase is also shown in the case of the silicofluoride hides where bacterial activity would have been curtailed or even stopped altogether. Since it has been shown that the development of volatile nitrogen parallels to a certain extent that of the extractable nitrogen[11] and in any case gives a clearer picture of the degree of putrefaction, i. e. the efficiency of the cure, the discussion will be based on the curves for volatile nitrogen shown in Fig. IV.

At the end of curing (0 weeks' storage) it is obvious that the only hides which had sustained any appreciable attack are those controls which had been cured for 30 days. The shorter the curing period, the less the bacterial attack had been. For the silicofluoride hides a value of 0.13 per cent was obtained, which indicates that some bacterial action had already set in prior to the application of the preservative. For most of the hides used in this work a period of about six hours elapsed between flaying and salting.

As the storage period increased for the silicofluoride hides there was a very slight increase in the development of volatile nitrogen from 0.13 per cent at the end of curing to 0.17 per cent after seven weeks' storage. The length of the curing period does not seem to have affected the development of volatile nitrogen to any appreciable extent. It is probable that the sl ght increase during storage is due to the action of the salt on the proteins, whereby they become more readily soluble, thereby allowing better extraction. In the controls, however, a different picture is obtained. Here the rate of volatile nitrogen development was quite fast for all the hides, but it is much faster the longer the hides had been in cure. In other words, hides cured for 30 days are more subject to bacterial deterioration during subsequent storage than hides cured for three days only.

This phenomenon is in keeping with all theoretical considerations regarding the curing process. During curing bacterial damage to hides is mostly due to the action of anaerobic bacteria which can only live in the absence of air. This condition exists in the centre of a stack of tightly-packed hides, especially if there is not too much excess salt. Along the edges of the stack, and in the centre as well when excess salt is applied, aerobic bacteria, which require fresh air for propagation, will cause damage. For this reason red heat, caused by aerobic bacteria, is usually confined to the edges of the stacks or to hides with excess of coarse salt present.

The second principle to be taken into account is that bacterial development under a given set of conditions always takes place in three definite stages.

During the first stage the bacteria have to adjust themselves to the new environment, in this case to living in high concentrations of salt. Now follows the stage of propagation and growth, the duration of which cannot be determined from the present work. The products of bacterial activity show a faster rate of development than during the adaptation stage. The final phase is reached when the rate of growth equals the rate of death, the latter due to the development of a high concentration of products toxic to the bacteria. It would seem that this stage has not yet been approached in the present experiment.

Finally, it is a well-known fact that many bacteria live symbiotically, i. e. two or more strains of bacteria may live together for mutual benefit. One strain may, for example, digest the protein only to a certain state and the second, which requires its food in exactly this condition, will continue the breakdown of products which would otherwise have become toxic to the first strain.

It is clear from the varying amounts of volatile nitrogen present at the end of curing that the bacteria have reached varying stages of development. When the stacks are now opened it is probable that all the anaerobic bacteria which might have been thriving in the centre of the stacks will be killed by the fresh air and that fresh inocculation of the stock with aerobic bacteria must occur. These bacteria now again have to adapt themselves to living under the conditions of concentrated sodium chloride solutions. Along the edges of the stack large numbers of aerobic bacteria have meanwhile been living for the duration of curing and infection can spread rapidly. Obviously in those hides where adaptation had progressed furthest during curing, i. e. the 30-day hides, the rate of growth must be fastest. In addition there will be more available foodstuffs present in those same hides as a result of bacterial activity prior to opening of the stacks, hence the bacteria can develop even faster. Therefore the rate of bacteria activity, as measured by the presence of volatile nitrogen, during the storage period will be faster in the 30-day hides than in the 3-day hides. This means that a 3-day cure is better than a longer cure. If all the hides were to be kept for a very long period, it is quite probable that the amount of nitrogen will become uniform for the hides from various cures, but it is impossible that the 3-day hides can ever be subject to more deterioration through bacterial action than the 30-day hides, as claimed in some quarters.

From this work it must be obvious that, from the point of view of the inherent quality of the cured stock, there is no necessity of salting hides for longer than three days and that, in fact, longer curing can only result in increased danger to the hides. Furthermore, it must also be clear that re-salting of hides in the tannery hide store, without the addition of a powerful antiseptic such as sodium silicofluoride, cannot prevent or even minimize bacterial

action when once started, provided the residual moisture in the hides has been previously saturated with salt.

The Limed Yields

In the beamhouse a check was made on the effect of the different cures upon the limed stock, the limed unfleshed yield on cured and green weight being taken into account apart from general observations referred to already. As will be seen from Table I the limed yield on cured weight increases with increasing length of the curing period for both series, being slightly lower for the silicofluoride hides than for the controls. This is to be expected, since soaking and liming constitutes a reversal of the dehydration process of curing. As long as the stock does not become excessively dry, as in dry-salted or sun-dried hides, it must take up roughly the same amount of moisture during soaking and liming, based on the green weight and must therefore show higher yields the higher the shrinkage during curing had been.

Limed yields on green weight do not take into account the curing shrinkage and should therefore be the same for all the hides unless some change has set in due to the different curing periods or the different treatments. It will be observed in the controls that the limed yields on green weight do not vary with the length of the curing period. The same holds true for the silicofluoride series, but there is an indication that these hides have taken up more moisture, i. e. have swollen more, than the controls. The difference is about 1 per cent only. See also Kritzinger[8].

These experimental hides had been treated as mixed packs in the tannery in such a way that control and silicofluoride hides went through the same pits and solutions. It was therefore decided to study this point further. For this purpose two stacks of 120 hides each were cured for six days, one stack as control and the other with 2 per cent silicofluoride added to the salt. The packs were divided in half and sent to two tanners. Tanner A treated the two packs of control and silicofluoride hides separately and reported a limed yield of 124.7 per cent for the silicofluoride hides as compared to 121.3 per cent for the controls, based on green weight and without fleshing. The difference is therefore over 3 per cent as compared to the previous results (also by Tanner A) were the difference was about 1 per cent. Tanner B mixed the two packs for soaking and liming, using a different process from Tanner A, and reported limed yields of 123.4 per cent and 122.4 per cent on green weight for the silicofluoride and control hides respectively.

It would thus appear from these results that the effect of the silicofluoride in increasing the limed yields is carried over from silicofluoride hides to control hides when they are processed together. A third experiment was conducted to verify this.

Two stacks of 192 hides each were built, one as control and the other with silicofluoride added to the salt, curing lasting for only six days. The hides

were now shipped to a tanner and kept in the bundled condition for four weeks before processing. From each group 96 hides were taken and divided into two batches of 48 each, the four batches thus obtained being processed separately through soaking and liming. The remaining 96 hides from one group were mixed with the remaining 96 from the other and the mixed lots divided into four batches of 48 each for processing as mixed lots by the same methods as for the unmixed. The fleshing operation was again omitted and the hides weighed to determine the limed yield on green weight. The results were as follows:

TABLE II

The Influence of Sodium Silicofluoride on the Limed Yield on Green Weight

	2% silicofluoride added to salt	Control Treatment
Processed separately		
Lot 1	126.8%	124.8%
Lot 2	126.4%	124.5%
Processed as mixed lots		
Lot 3	126.0%	125.3%
Lot 4	126.0%	125.0%

From these results it is clear that the addition of sodium silicofluoride to the curing salt results in increased limed weights of the stock. It also follows that when silicofluoride-treated and control hides are processed together through the beamhouse, the silicofluoride hides show a smaller gain in weight but the control hides show an increased gain, i. e. the effect of the sodium silicofluoride has spread itself over all the hides. This effect of the sodium silicofluoride is probably due to its dispersing effect upon the globular proteins[10], whereby the stock is opened up more in the soaking process. The addition of small amounts of sodium silicofluoride to the soak liquor might thus be advantageous to the processing of stock.

Summary and Conclusions

1. The loss in weight from the green to the cured state decreases rapidly as the curing period for wet-salted hides is shortened.

2. When 2 per cent sodium silicofluoride is mixed with the curing salt, the shrinkage figure is from 2 per cent to 3 per cent lower than for corresponding control-salted hides.

3. After only three days in cure the residual moisture in the hides is completely saturated with sodium chloride. Any further loss in weight is therefore due to the flowing away of saturated brine out of the hides. Some loss might be due to atmospheric drying along the edges of the stack.

4. Hides cured for varying periods do not show different degrees of weight loss during transportation.

5. The amount of salt which can be shaken free from hides after transportation is not dependent upon the length of the curing period and easily amounts to about one pound per hide.

6. Variations in the length of the curing period do not affect the rate of weight loss during subsequent storage without salt. This is due to the fact that most of this loss is the result of atmospheric drying.

7. As the curing period is increased the amount of volatile nitrogen developed in the hides, as an indication of bacterial activity, increases rapidly. Where sodium silicofluoride is used with the salt the volatile nitrogen remains a minimum.

8. When hides, cured for varying periods, are stored as in tanneries without salt for a further seven weeks, volatile nitrogen will develop faster the longer the hides had been in cure prior to storage. Here again hides treated with sodium silicofluoride do not show such an increase in the rate of bacterial breakdown of the proteins. A curing period of three days is therefore preferable to one of say 30 days.

9. The limed yield on green weight does not vary with the length of the curing period.

10. Limed yield on green weight is greater for hides treated with salt containing sodium silicofluoride.

11. Limed yield on cured weight varies proportionally with the curing period, in other words with the degree of shrinkage during curing.

12. Merely judging by appearance, handle and smell it is very difficult to distinguish between hides cured for 3 and 30 days respectively, except that the former will appear somewhat wetter and will not show a strong putrefactive odour.

Acknowledgments

This work could not have been done without the much valued assistance of Messrs. Consolidated Hide and Skin Traders Ltd., Bagshaw, Gibaud & Co., Karroo Produce Exchange Ltd., Sutherlands Tannery Ltd., and Transvaal Associated Hide & Skin Merchants, Ltd.

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BOOK NOTICE

Ion Exchangers in Analytical Chemistry. Olof Samuelson. XVIII + 291 pages. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 16, N. Y. 1953. $6.50.

This is the first book devoted exclusively to the use of ion exchangers for analytical separations. Ion exchange methods have become increasingly important in the last decade and the analyst wishing to consult earlier published works or desirious of investigating new fields of use will find the present book of great value. After a short introduction, the next 70 pages are devoted to a theoretical discussion of ion exchangers, covering such topics as the fundamental properties of ion exchange resins, equilibria, kinetics, and column operation. Techniques of ion exchange separations and chromatography are described in the second section (45 pages). The type and particle size of the resin, column dimensions, flow rate, concentration, acidity and temperature of the solution to be analysed are discussed. The remainder of the book describes specific applications in the fields of inorganic, organic, and biochemical analyses. Detailed descriptions of the applications are not generally given, although in some cases column dimensions, flow rates and concentrations are included. Tables showing the accuracy and precision of results are frequently given. Excellent bibliographies are included at the end of each chapter. An appendix giving the characteristics of a number of commercially available resins is included. R. S. A.

ABSTRACTS

Ironwood of Malabar as a Tanning Material. By P. H. Rao, *Science and Culture (India)* **18**, 243 (1952). Through *Chem. Abst.* **47**, 5147 (1953). Analysis of ironwood ("Irumbagan") bark gave tannin 17.9, soluble nontannins 8.7, and tannin: nontannin 2.05. Tannin and purity values are inferior to those given in the literature. Leather produced from ironwood extract is objectionably dark.

The Tannin of the Bark of *Salix Koriyanagi*. I. By K. Sakata and J. Kishimoto. *J. Japan Forest Soc.* **34**, 373 (1952). Through *Chem. Abst.* **47**, 5147 (1953). The bark of *Salix koriyanagi* contains about 0.5 per cent tannin (air dry basis), classified as catechol

tannin by Proctor's method. The tannin content decreases with elevation of the bark on the trunk. The relation between the amount of extract, tannin and the conditions (temperature and time) of extraction was determined.

Rational Methods of Sulfitization of Tannin Extracts. By M. N. Krasukhin. *Legkaya Prom.* **11,** No. 10, 38 (1951). Through *Chem. Abst.* **47,** 5148 (1953). The following conditions are optimum: (1) Oak extract is treated with 5 per cent by weight (of dry extract) of crystalline sulfite for 4 hours at 90°. Insolubles are 7.3 per cent; loss of tannin 1.3 per cent. (2) Spruce and willow extracts are treated with 6 per cent crystalline sulfite for 3-4 hours at 90-100°. Yield of tannins is 106.7 per cent (spruce) and 110.9 per cent (willow).

Characteristics of Syntan AN Made with Oleum. O. S. Apanaev. *Legkaya Prom.* **11,** No. 8, 26 (1951). Through *Chem. Abst.* **47,** 5148 (1953). Analysis of Syntan AN prepared with oleum containing 20 per cent free SO_3 showed a smaller decrease in content of nontannins than was to be expected from the smaller amount (14.6%) of monohydrate required to complete the process. This difference was traced to the method of analysis. The Russian specification OST - 35017 requires that the analytical solution contain 3.8 - 4.5 g. dry residue per liter, corresponding to 1.45 - 170 g. of substance adsorbed by hide powder. This is valid for syntan prepared with 92-96% H_2SO_4. Existing specifications should be clarified to cover the concentration of the analytical solution of syntan prepared with oleum.

Thermal Endurance of Dry Collagen. By G. I. Kutyanin. *Kolloid. Zhur.* **15,** 36 (1953). Through *Chem. Abst.* **47,** 5148 (1953). Strips of hide or leather, 3 mm. wide and 31 mm. long, were loaded with 5 g. and heated dry in a metal bath. The length l of the strips did not change below about 90°. At 210-225° l decreased rapidly, and at higher temperatures decomposition started. Between 90° and 210° the change in l varied with the initial water content Q of the sample; when Q was small, the decrease of l below 210° also was small; and when Q was large l decreased greatly at, for example, 120° (because of dehydration), and the decrease in l at 210-225° was small. The final l at 225° was almost independent of Q. The temperature at which l of wet samples first decreased was raised by tanning, but the temperature of the final decrease of l was identical for hide and leather and depended but little on the animal (goat, cow).

Investigation of Tanning Systems Containing Complex Chrome Salts with Naphthalene Sulfonic Acid. By N. S. Fokina, I. N. Bulanzhe and M. P. Kotov. *Legkaya Prom.* **11,** No. 12, 32 (1951). Through *Chem. Abst.* **47,** 5149 (1953). Three extracts contained mostly anionic complexes, two extracts contained mostly cationic complexes. All of the extracts can be used for tanning. Extracts containing complex chrome salts with naphthalene sulfonic acid proved superior to ordinary extracts used in chrome tanning. Best results were obtained with extract prepared by dissolving one part of $Cr(OH)_3$ in one part of sulfonic acid. An excess of sulfonic acid or its condensation products lowers the quality of the leather.

New Mechanism in Chrome Tanning. By I. P. Strakhov. *Legkaya Prom.* **11,** No. 12, 23 (1951). Through *Chem. Abst.* **47,** 5149 (1953). Theory of trans-effect leads to the conclusion that coupling of chrome compounds by collagen is greater when half of the

coordination points in the inner sphere of the chrome belong to more active trans-radicals than water. Investigation has shown that cationic compounds of basic chrome sulfate used in tanning, which have a greater number of labile molecules, have a greater capacity for combining with albumins than cationic chrome chloride and anionic chrome sulfate.

Some Reactions of Esterified Collagen. By K. H. Gustavson. *Acta Chem. Scand.* **6,** 1443 (1952). Through *Chem. Abst.* **47,** 5149 (1953). The COOH groups of collagen (*I*) were esterified with MeOH 0.1 *N* with respect to HCl; the esterified collagen (*II*) contained 0.79 meq. MeO per g. *I*, and its HCl-binding capacity was reduced by 0.77 meq. of H ion; *II* commenced to shrink at 37°, compared with 62° for *I*. Dilute solutions of basic chlorides, perchlorates, and sulfates of Cr, containing cationic Cr complexes, showed almost no affinity for *II*. From concentrated solutions of basic Cr compounds of the type $Cr_2(OH)_m\ (SO_4)_n \cdot Na_2SO_4$ containing a large percentage of nonionic and anionic Cr complexes, *II* fixed small amounts of Cr. From solutions of sulfite-sulfato-Cr complexes and of basic Cr sulfates complexed by means of the phthalate, with noncationic Cr as the chief constituent, *II* fixed irreversibly large amounts of the complexes. The results proved the dominating function of the ionic CO_2H groups of *I* in fixing cationic Cr complexes.

Vegetable Tanning Under Conditions Prevailing in Argentina. Comparison of Relative Merits of Ordinary and Sulfited Quebracho Liquors. By H. Giovambattista, A. A. Giacomi and W. O. Palavecino. *Lab. En sayo Materiales e Invest. Tecnol., Prov. Buenos Aires.* Ser. II, No. **45,** 5 (1952). Through *Chem. Abst.* **47,** 5150 (1953). To study the effects of the high mobility of sulfited quebracho combined with the greater fixing power of the raw extract, a series of parallel tests were run: (a) initial use of the sulfited extract followed by final treatment with the raw tanning agent; (b) a tanning procedure following current industrial practice, with the use of the sulfited material alone. Under (a) the skins were tanned for 2 days in a sulfited liquor of 0.1 - 1.0° Bé; 2 days at 1.5 - 2.5° Bé, and 3 days at 6.0 - 7.0° Bé. This treatment was followed by tanning in non-sulfited quebracho at 7 - 9° Bé. at 30°C. for 6 days. Natural pH was maintained in each case except that lactic acid was used to bring the pH of the raw extract to that of the sulfited. Under (b), similar skins were treated under like conditions of pH, temperature, and concentration with sulfited liquor alone. Results of 14 tests showed that the dual treatment brought about an 11 per cent increase in fixed tannin and a 15 per cent increase in the degree of tanning, while solubles were reduced 2.5 per cent.

The Electric Resistance of Leather. L. D. Pezzo. *Cuoio, Pelli, Mat. Concianti,* **28,** 455 (1952). Through *Chem. Abst.* **47,** 5150 (1953). The electrical resistance was determined on leather samples conditioned at 20° and 65% R.H., with the following results (in ohms $\times$ cm. x 10^{-3}; vegetable sole 0.98 - 2.16; vegetable upper 2.37; chrome-vegetable 7.95; chrome leather with 14% fat 4.33; chrome upper 15.33 - 34.18. Electrical resistance increased noticeably in defatted and washed leathers: original samples 0.61 - 2.63, defatted 0.74 - 4.14; defatted and washed 16.56 - 100.50. Resistance is slightly higher if measured with the positive pole to the flesh side than when measured in the opposite direction.

Water Permeability of Russet Uppers. By G. I. Kutyanin and V. G. Suchkov. *Legkaya Prom.* **11,** No. 11, 19 (1951). Through *Chem. Abst.* **47,** 5151 (1953). An increase in water resistance can be obtained by tanning the middle layer of the skin to a lower

shrinkage temperature than the outer layers. The middle layer will be almost exclusively vegetable tanned while the outer layers will be both chrome and vegetable tanned. This will not interfere with subsequent improvement in heat stability of leather through additional chrome tanning of outer layers.

Effective Method of Utilizing Leather Trimmings. By N. I. Kashkin. *Legkaya Prom.* **11,** No. 9, 8 (1951). Through *Chem. Abst.* **47,** 5151 (1953). Leather trimmings are converted into a carburizing agent with $CaCO_3$. The trimmings are heated in the absence of air for 5 - 8 hours in a muffle furnace with a yield of 58 - 60% amorphous C. This is then mixed with $CaCO_3$ in the ratio of 3:2. The gases from the furnace are condensed and recovered. Preliminary investigations indicate that the tar can be used in making dyes.

Effect of Conditions of Liming of Fleshings on the Quality of Glue. By V. N. Kolesnikov. *Legkaya Prom.* **11,** No. 9, 37 (1951). Through *Chem. Abst.* **47,** 5153 (1953). Tests were made with second machine fleshings from cow hides. Liming should be done with a liquid coefficient of 1 in vats and 0.7 in piles; milk of lime of 5° Bé. plus 2.5 g. Na_2CO_3 per liter is used.

The Chemistry of Tanning. I. Formation of Peroxide Groups in the Oils. By J. Glavind and J. W. Pedersen. *Acta Chem. Scand.* **6,** 451 (1952). Through *Chem. Abst.* **47,** 5707 (1953). Oils extracted from hides in various stages of tanning were analyzed to test the suggestion that the reactive groups in the oil tanning process are peroxide groups formed by the action of atmospheric oxygen on the unsaturated constituents of the oils. Data on marine oils sampled during the tanning of sheep skins show that there is a definite lowering of the iodine value, and an increase in the peroxide value, with maximum occurring 10 to 12 days after milling of the stock. The data are in accord with the supposition that peroxide formation plays a decisive role in the oil tanning process.

The Chemistry of Oil Tanning. II. The Chemical Nature of the Bonds Between Peroxidized Fats and Collagen. By J. W. Pedersen and J. Glavind. *Acta Chem. Scand.* **6,** 453 (1952). Through *Chem. Abst.* **47,** 5707 (1953). The peroxides, which have been shown to be the reactive species in oil tanning, are effective only at pH values below 5.5. Skin and oil-tanned leather were analyzed for total nitrogen and for free amino nitrogen. About 0.14 millimole of fatty acid is taken up per gram of dry leather so that the leather contains 4.2 per cent oil. The free amino groups change only from 0.38 millimole per gram of skin to 0.35 millimole per gram of leather; thus these groups cannot be involved in the tanning reaction. Fat peroxides (or hydroperoxides) are known to react with organic acids, and an analogous reaction may take place in oil tanning, leading to fatty acid-collagen linkages of ester character. Saponification of tanned hide liberates 0.31 millimole of carboxyl groups per gram of leather, indicating that one mole of unsaturated fatty acid combines with two carboxyl groups. The leather was detanned during saponification. Apparently the hydroperoxides form bridges between the carboxyl groups of adjacent collagen peptide chains.

The pH of the Pickle in Tanning with Black Acacia Tannin. By L. Anusz, N.B. de Oliveira and C. C. Oliveira. *Anais Assoc. Quim, Brasil* **10,** 346 (1951). Through *Chem. Abst.* **47,** 5707 (1953). Pieces of limed, unhaired calf skin were washed, delimed

with 0.5 per cent sulfuric acid on the skin weight, bated for 3 hours with 0.8 per cent Oropon XXS at 35°, and pickled in 6 times their weight of 10 per cent salt solution with 0, 0.2, 0.4, 1.3, 0.7, 1.0, 1.1, 1.3 and 1.4 per cent sulfuric acid, establishing pH values of 5.4, 5.0, 4.7, 1.5, 4.0, 2.3, 2.7, 3.1 and 1.9. Tanning was done by discarding two thirds of the pickling liquid, and adding water and black acacia tanning extract in such amounts as to have liquor to skin ratio equal to 6, with successive concentrations of 0.6, 1.5, 2, and 2.5 per cent tannin. Tanning was completed in 4 days. The skins were pressed with 5000 pounds per square inch pressure, washed a half hour, dried and analyzed. The pH values of the aqueous extracts of the leathers were 3.7 - 4.4 for stock pickled at pH 5.4 - 4.7 and 2.6 - 2.4 for stock pickled at pH 4.0 - 1.5, respectively. Shrinkage temperature declined with pickle pH from 85 to 70-71°. Fixed tannin per 100 parts collagen was 40-46 for all leathers except those pickled at pH 2.7 - 2.3, for which values of 67 and 66 are reported. Water soluble matter per 100 collagen was 23 - 20 for leathers pickled at 5.4 - 5.0, and 28-35 for the other leathers. Ratio of tan to nontan in the aqueous extract was about 2.5 to 1 for leathers pickled at pH 1.9 and 1.5, and about 2 to 1 for the other leathers. Tensile strength varied from 235 to 292 kg. per square cm., and was lowest for leathers pickled at pH 2.7 and 3.1. pH values did not affect the rate of tannin penetration.

Analytical Procedure for Pancreatic Enzymes. By J. F. Llonch. *Afinidad* **29,** 482 (1952). Through *Chem. Abst.* **47,** 5708 (1953). Enzyme-containing products used in the leather industry can be evaluated by a modified Fuld-Gross method.

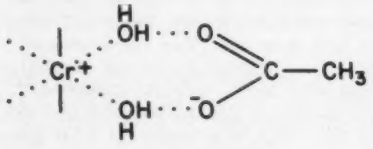
The Reaction of Chrome Complex to the Ion Exchange Resin. I. The Reaction Between Amberlite IR - 4B and Oxalato Chromate Complex. By Y. Inone, A. Kawamura, K. Wada and H. Okamura. *Japan Analyst* **2,** 21 (1953). Through *Chem. Abst.* **47,** 6165 (1953). Ion Exchange behavior of pure $K[Cr(C_2O_4)_2(H_2O)_2]$ *(I)* and $K_3[Cr(C_2O_4)_3]$ *(II)* was investigated as an aid to the analysis of chrome tanning liquor. The column of regenerated Amberlite IR-4B was treated with NaCl, Na_2SO_4, Na_2HPO_4, $NaNO_3$, HCl, H_2SO_4, H_3PO_4, HNO_3 AcOH, or $(CO_2H)_2$ to form their salts. Then the solution of *I* or *II* (0.1% as Cr_2O_3) was passed, and the effluent was analyzed for Cr and $(COOH)_2$. The best result was observed on the resin treated with $AcOH_3$, and the leakage of Cr depended on the kind of anions by which the resin was treated and was independent of the degree of washing or the existence of the other ions. The resin treated by acids gave better results than that treated by salts, and *II* was more easily exchanged than *I*.

Leather and Tanning Agents. VI. Ultramid 6A as Adsorbent in Tannin Analysis by the Filter Method. By H. Batzer. *Makromol. Chem.* **8,** 185 (1952). Through *Chem. Abst.* **47,** 7806 (1953). The following tannin values were found in extracts analyzed by the filter method and with hide powder and with Ultramid 6A: quebracho 45.8 and 44.4; chestnut 73.7 and 72.8; valonia 68.4 and 65.0; oak 69.7 and 66.7; mimosa 71.3 and 71.6; and sumac 31.1 and 29.2 per cent respectively. Ultramid 6A can be used in the filter method instead of hide powder.

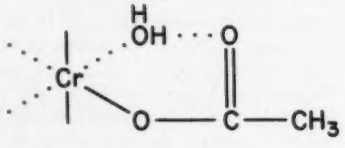
Tanning Experiments with Polyamides. By A. Küntzel. *Makromol. Chem.* **8,** 178 (1952). Through *Chem. Abst.* **47,** 7806 (1953). The author replied to the article by Batzer (see preceding abstract), stating that vegetable tanning has never been considered a primary valence bonding; also, that there are several types of hide protein reactions.

Critical Notes on Moisture Determination by Means of the Oven Drying Method. By E. Raabe and J. Abramovna. *Prace Plocowek Nauk.-Badawcz. Ministerstwa Przemyslu Chem.* pg. 47 (1952). Through *Chem. Abst.* **47**, 7806 (1953). Studies of leather conditioned at 65 per cent R.H. for 1-18 days show that a constant moisture content is reached after 3 days. Certain experimental discrepancies were ascribed to the method of drying and the method of tanning. Drying at over 100° is undesirable as it leads to excessive error. It is believed that drying at 100° for 4-5 hours is adequate. Experiments were carried out on leathers tanned with vegetable tannin, chrome and syntans. The drying conditions studied were oven drying at 80° to 150°, at 10° intervals, drying over P_2O_5, and xylene distillation.

Formation of Simple Masked Chromium Complexes. VI. The Constitution of Organic Masked Chrome Compounds (Chromium Formate, Acetate and Oxalate). By A. Küntzel, H. Erdmann and H. Spahrkäs. *Das Leder* **4**, 73 (1953); [*This Jour.* **47**, 799]. In pure chromium sulfate systems, only sulfato complexes with a green-blue color are formed, but formiato and acetato complexes are of two types, a violet and a green type. If sodium acetate is added to violet hexaquochromic chloride solution, there is an immediate reaction with formation of a yellowish green basic salt. In addition to a buffering action a complex is formed. This is shown by the fact that the conductivity titration curve (conductivity versus ml. N/200 sodium hydroxide) rises at once, whereas without sodium acetate the curve first drops then remains constant during precipitation of the chromium. The acetyl radical is not attached directly to the chromium atom but through the aquo group by a sort of hydrogen bond, as is shown in I.

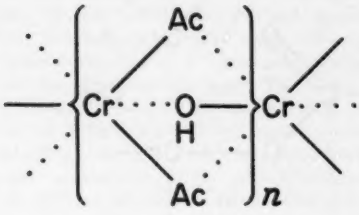


I

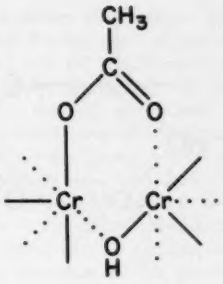


II

On aging, a secondary reaction takes place in two phases. In a few hours there is a color change from greenish to blue-violet, then after several months to blue-green. During this time the conductivity titration curves, taken after ½ hour, 2 hours, 1 day, and 1 year, become steeper; conductivity increases more rapidly (as sodium hydroxide is added) the older the solution. In the first phase a true complex (II) forms; one (or more) aquo groups leave complex I and one (or more) acetato groups enter the coordinate sphere of the chromium atom. This complex is more stable and conductivity therefore decreases. There are approximately 2.75 acetato groups per chromium atom in complex II, with equilibrium between tri-, di-, and mono-acetato complexes. In the second phase (color change violet to green) the mononuclear diacetato-mono-hydroxo-complex aggregates to chain-like polynuclear compounds in which each pair of chromium atoms is bonded by 2 acetato and 1 ol bridge (complex III).

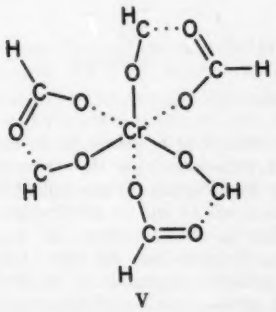


III

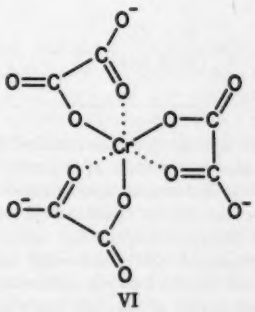


IV

This coupling is quite stable because of the 6 membered ring (IV) which is formed by the acetato group; this ring is more stable than the 5 membered ring II. If mixtures of acetic acid, sodium acetate, and sodium hydroxide are added to 0% basic chromium chloride solutions (0.1% Cr), keeping the ratio of 6 acetate ions per chromium atom, and using amounts so that the pH values of the solutions varied from 2.2 to 6.9 after 4 months, the color change from violet to green (second phase change) is found only in the weakly acid range, approximately between pH 3 and 5. In the neutral range a stable, violet complex forms in which the aquo group of II is replaced by a hydroxo group; no green complex forms. Complexes do not form in the acid or alkaline zones. Formate differs from acetate in that it ionizes to a greater degree and less formate enters the complex, for example 1.7 groups per chromium atom instead of 2.75 as with acetate. Formate is a better commercial masking agent because it has less tendency to form compounds that are inactive as regards tanning ability. In concentrated solutions hexa-formato-sodium chromate is formed. The formato groups are joined by hydrogen bonds to form 7 membered rings as shown in V.

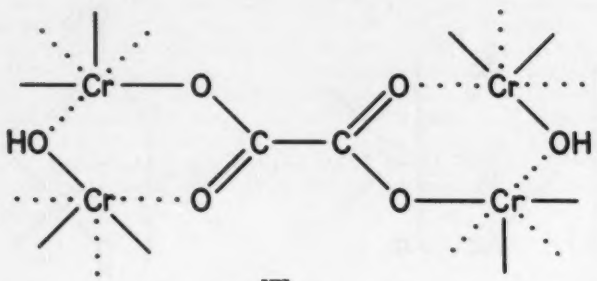


V



VI

Oxalate at first reacts like acetate except that it is joined through aquo groups to 2 chromium atoms instead of 1; then di- and tri-oxalato complexes form. On heating with 6 or more equivalents of oxalate per chromium atom the tri-oxalato complex (VI) forms. The aquo groups in the mono- and di-oxalato complexes tend to hydrolyze after which the complexes aggregate to compounds with ol and carboxyl bridges (VII) which are quite stable because of the 6 membered rings.



VII I. D. C.

The Kinetics of Chrome Tanning. Comments on the Work of P. Stanley Briggs. By H. W. von Thaden. *Das Leder* **4,** 145 (1953). During the period 1945-51, P. S. Briggs published a series of articles *(J. Soc. Leather Trades' Chemists* **46,** 140 and **47,** 70) dealing with the kinetics of chrome tanning and assuming that leather quality could be controlled best by following liquor exhaustion. He developed the formula

$$\frac{d\,[Cr]}{dt} = f\,[Cr] = -A\,[Cr]^m$$

which, if $K = A(m\text{-}1)$ and $n = m\text{-}1$, can be transformed to $Kt = [Cr]^{-n}\text{-}1$, where [Cr] is concentration of chrome, t is time, d is derivative, and K, m, n and A are constants. The following values for chrome retanning of vegetable leather are typical:

	Bend	Belly
n	4.5	2.15
K	1.38	1.29
Half time	15.7 hours	2.67 hours

The half time is the time required for half of the chrome to be taken up by the hide. Briggs gives many data of this type but they show little more than the tanner already knows. At the start of tanning chrome concentration drops rapidly. Briggs calls this "contact drop" caused by rapid surface tannage (a chemical effect) and by dehydration of the skin (a physical effect). The chemical effect is made up of two factors: (1) a tanning (combination of tannin and skin) and (2) diffusion of tannin into the skin. Equations are derived for the limiting cases where diffusion is either (1) negligible or (2) very large compared to rate of tanning, but where tanning and diffusion are equal the equation can not be used because of unknown factors. The concentration of chrome in the surface layer is not known, the thickness of this layer is constantly changing, the effect of temperature on diffusion and reaction rate differs, etc. The empirical exponential function for chrome liquor exhaustion correctly describes qualitatively certain effects such as basicity changes, dilution, masking, etc., but a quantitative evaluation of the curve with calculation of function constants is useless because tanning is a complex superposition of several processes. I. D. C.

A New Apparatus for Measuring the Air Permeability of Leather. By F. Föhr. *Das Leder* **4**, 150 (1953). The Bergmann apparatus for measuring air permeability [*This Jour.* **24**, 150 and **25**, 38] has been modified, retaining only the test chamber which consists essentially of two metal cones between which the leather is clamped. Air under pressure was supplied by a water or electric pump but any available source with a suitable reducing valve might be used. The author's pump supplied 9 liters of air per minute at a maximum pressure of 400 millimeters of water. With a water pump, a wash bottle containing sulfuric acid of the proper concentration should be used to reduce the relative humidity to some desired level. An adjustable vent to regulate air pressure and a manometer are connected to the air supply through tee tubes in the rubber tube which conducts the air from the pump to the test chamber. The air leaving the test chamber is measured with an experimental gas meter of the wet type. The advantages of this modification are that there are no water reservoirs to fill, no breakable glass parts, the direction of flow through the leather can be easily changed, and measurements can be continued for an indefinite time and changes made in temperature and relative humidity of the air during a run. The following table shows average air permeability, in cc. per minute, at different pressures (in millimeters of water) with air entering the grain and the flesh sides of the leather.

Pressure	50	100	150	200	250	300	350	400
Grain	70.8	151	232.0	314	399	478	566	642
Flesh	72.0	153	234.6	318	404	488	579	660
Difference	1.2	2	2.6	4	5	10	13	18

Bergmann stated that for a given leather specimen the air transmitted per unit area (25 square centimeters) in unit time (1 minute) divided by the air pressure (millimeters of water) was a constant. This is not strictly true; the value increases slightly as pressure increases. I. D. C.

Determination of the Basicity of Zirconium Salt Solutions. By A. Küntzel and K. Rosenbusch. *Das Leder* **4**, 153 (1953). The determination of the basicity of zirconium sulfate solutions by hot titration with 0.1 normal sodium hydroxide and phenolphthalein does not give correct results because of precipitation of basic zirconium sulfate. Addition of an excess of alkali and back titration of the excess is also in error because of irregular absorption of acid or alkali by the zirconium oxide precipitate. If an excess of sodium fluoride is added a hexafluoro zirconium complex is formed and hydroxyl is forced out of the basic salt and can be titrated. The hydroxyl is reacted with an excess of standard acid and the excess acid titrated with iodide-iodate and thiosulfate. The method is as follows: To the zirconium salt solution containing 2-5 milliequivalents of zirconium, add 10 cc. of a 1 normal sodium fluoride solution. Add enough N/10 hydrochloric acid to liberate iodine after addition of the iodide-iodate solution (this iodate solution must be freshly prepared; iodine if present must be removed with thiosulfate; 0.4 grams of KI and 0.1 grams of KIO_3 are sufficient to titrate 25 cc. of 0.1 N acid). Add an excess of N/0 thiosulfate, boil for a short time with exclusion of carbon dioxide, cool, and titrate the excess thiosulfate. The difference between thiosulfate used and acid added is equivalent to hydroxyl liberated when fluoride was added. Basicity is 100 times equivalents of acid used divided by equivalents of zirconium. In a solution of pure zirconium oxychloride, $ZrOCl_2 \cdot 8H_2O$, zirconium and chloride (Volhardt) were determined and basicity calculated

as 49.6%; found by the fluoride method, 48.3%. In a technical preparation the corresponding values were 44.2% and 44% resp. For a solution of Zirkotan N a basicity of 40.6% was found by analysis for the elements and 39.2% by the fluoride method.—I.D.C.

The Existence of Chloro-Chromium Complexes in Chromium Chloride Solutions. By A. Küntzel, H. Erdmann, H. Spahrkäs and H. W. v. Thaden. *Das Leder* **4**, 169 (1953). In highly basic chromium chloride solutions, 70-90 per cent of the chromium salt is not retained by ion exchange resins. Gustavson's explanation of this fact [*This Jour.* **47**, 151] is that the chromium is present in an uncharged chloro-hydroxo-complex. It was recently [*This Jour.* **47**, 799] pointed out that this was not probable. Gustavson has reviewed the whole field [*This Jour.* **48**, 265] but most of the work cited was done on 33 per cent basic chromium chloride solutions, in which the presence of chloro-complexes is not disputed, rather than on highly basic solutions. The evidence indicates that the particle size is too great for the complex to penetrate and be retained by the ion exchange resin rather than that the complex is uncharged and therefore not absorbed. Uncharged particles should not tan whereas these highly basic complexes do tan. When green dichloro-chromium chloride was dissolved in water (chromium concentration N/3460) and titrated with sodium hydroxide, the titration curves at first showed an initial rise (increased conductivity) as a result of replacement of chloro-groups by aquo groups in the complex. This initial rise became less with time and after 12 or 15 hours changed to a fall in the curves indicating decreased conductivity due to neutralization of acid from hydrolysis. After enough alkali had been added to form a 33 per cent basic salt all curves followed the same course, indicating absence of chloro complexes. By electrophoretic measurements with the Antweiler apparatus a moving and a stationary boundary were found. By varying the salt (NaCl) concentration, (that is, the sodium to chromium ratio), the stationary boundary could be made to vanish, thus showing it to be an "extragradient" and not an evidence of uncharged particles. Absorption by exchange resins from chromium chloride solutions decreased as particle size increased when solutions of various particle sizes were used. The size was made to vary by altering concentration during preparation of the solutions. If, because of high concentration or addition of sodium chloride, chloro-aquo-complexes are found in chromium chloride solutions, they are destroyed at once on addition of sodium hydroxide. On aging, disproportioning occurs with formation of ol compounds of higher basicity and hexaquo complexes of lower basicity. The latter are in equilibrium with a small amount of chloro-aquo complex, so that if aquo complexes are present a little chloro-aquo complex must also be present in the solution. If basicity is increased to the highly basic region then in both fresh and aged solutions only hydroxo compounds are to be found. Disproportioning produces ol complexes of higher and lower basicity but no aquo complexes. These basic compounds are stable because of their cationic nature but they are too large to diffuse into an ion exchange resin. I. D. C.

Proposed Tentative Method for the Examination of Leather Oiling Materials. By R. Schubert. *Das Leder* **4**, 177 (1953). For the analysis of fats there are several more or less official methods but it is not possible to analyze most of the present day fatliquors by these methods because they no longer are simple sulfated oils. Fatty material content of a sample is usually determined by the indirect method, that is by subtracting the sum of all nonfat components from 100 Constants for the fat (acid number, iodine number, etc.) can be determined only for solid fat mixtures, the fat in emulsions has been chemically modified so the constants do not have their normal values. Water in the oil can not be accurately determined by direct heating methods. The Karl-Fischer method [*This Jour.*

48, 327] is excellent but is not suitable for technical leather work. The proposed method is to distil 20-100 grams of sample, containing 2-10 cc. of water, in a reflux apparatus with graduated collection tube (Dean-Starke type of apparatus) with xylene or toluene. There is no tested method for volatile organic matter. The following 3 methods are proposed for trial: (1) To a 250 cc. short necked flask, add 10 grams of sample and 25 cc. of methanol and evaporate on a steam bath; add 2 10-cc. portions of methanol, evaporating each, then dry the flask and contents at 50°C for 2 hours. (2) Dry 10 grams of sample in a shallow glass dish, 80 millimeters in diameter, at room temperature (20-25°) in a vacuum desiccator over sulfuric acid or silica gel. (3) Dry 10 grams of sample in a shallow dish (80 mm. diameter) at 50°C for 24 hours. Volatile organic matter is the drying loss decreased by the amount of water found by distillation with xylene. Ether insoluble matter in water-insoluble, leather oiling materials may be determined as follows: Warm 8 grams of sample to 50°C then filter through a filter paper (Schleicher & Schüll No. 5891 black band) that has been dried at 100°, weighed, and reconditioned. Wash with 100 cc. of ether and dry at 100° to constant weight (twice 1 hour). If the material is a solid or paste, weigh 8 grams into a filter paper as before, fold the paper into a pocket, and thoroughly extract with ether in a soxhlet, then dry and weigh as before. After weighing, burn off the paper, moisten with hydrogen peroxide and ash. The extraction residue minus ash equals organic nonfat. Separate the emulsified and emulsifier fractions of water miscible materials as follows: Shake vigorously 2 grams of sample, 25 cc. of petroleum ether and 25 cc. of 50 per cent ethyl alcohol. Let stand, preferably overnight, until the layers separate (add 20 cc. of ethyl ether if necessary to obtain good separation). Draw off the alcohol layer and wash the ether layer with 25 cc. of 50 per cent alcohol. Distil off the solvent from the petroleum ether (or petroleum and ethyl ether) extract and from the combined water-alcohol extract in short necked flasks on a water bath. Dry the residues 2 hours in an oven at 50° and weigh. The ether extract is the emulsified fraction of the sample. Take up the alcohol extract in 25 cc. of water-free alcohol, filter through a weighed paper (see above), wash with 25 cc. of alcohol, dry the residue and filter at 100° and weigh. The alcohol insoluble residue is the mineral matter. The alcohol extract minus mineral matter equals the emulsifier fraction. To measure pH, add enough distilled water to 10 grams of sample to give a volume of 100 cc., shake, let stand 5 minutes, then measure pH with a glass electrode at 20°. Before each measurement rinse the electrode with ether. I.D.C.

The Occurrence of Gallnuts in Germany and the Requirements for their Formation. By F. Föhr. *Das Leder* **4**, 182 (1953). A sample of galls collected near Ludwigsburg during rainy weather had the following analysis by the filter method. Water 27.6%, insolubles 38.0%, nontannin 4.9% and tannin 29.5%. The tannin content is high even though there was evidence of mold due to high moisture in the sample, and the possibility that some tannin had been leached by rain. The mode of formation of galls and the possibility of cultivating them in Germany are discussed. I.D.C.

Combining Reactions Between Aromatic Substances and Protein Fibers. By Gerhard Otto. *Das Leder* **4**, 193 (1953). The reactions between aromatic compounds and proteins play important roles in tanning. Vegetable tannins, syntans, and organic dyes are aromatic compounds. Recently aromatic sulfo acids have been used for pickling because they do not swell the hide. The unusually wide variety of behavior of these aromatic substances has, however, hindered development of simple conceptions of how they combine

with proteins. Many syntans, dyes, etc., show a decided tendency to combine coordinately with protein fibers although they have no hydrogen atoms (OH or NH groups) to serve as electron acceptors or form bridges. Speakman and Elliot (Soc. Dyers Colourists, Symposium on Fibrous Proteins, 1946, p. 116) in a study of absorption of aromatic sulfonic acids by wool, found that the absorption increased as the aromatic portion of the sulfonic acid increased in size; also that this increase in absorption was true at the isoelectric point or above, so that coordinate forces were involved since electrovalence forces could not act. Bergmann et al (Collegium, 1930, p. 520) found that aromatic sulfonic acids did not swell hide or had a deswelling action so that in addition to electrovalence forces there must be other forces that give thermal stability. Cross linking, which prevents swelling, develops sooner the larger the aromatic portion of the molecule. Küntzel (Collegium, 1940, p. 500) found that phenol had a tanning as well as a swelling action on hide. If hide, which had been dehydrated so the chains were nearer together, was immersed in a solution of phenol in alcohol, then was removed and put in water before all of the alcohol had evaporated, a leather-like material resulted. Phenol has only one OH group but the benzene ring has several mesomeric forms and the dipoles thus formed can form cross links and stabilize the hide lattice. In the peptide group, the O-N dipole can change the sign of its charge depending on the sign of a neighboring dipole. Polyvinylpyrrolidon, 38 per cent of which consists of dipole active groups, cannot form covalent or electrovalent compounds but has affinity for dyes. The range of electrovalence forces is about 100 angstroms and of coordinate valence 2·5 angstroms. Molecules are drawn together by electrocalence forces, then joined (combined) by coordinate valences. If hydrogen bonds also form, the dipole bond is strengthened. Sulfo acids of naphthol swell hide less than those of naphthalene. The coordinating force of sulfanilic acid derivatives is strengthened by introducing electron donating groups (OH, NH_2). From syntan manufacture it is known that tanning power decreases as the number of sulfo groups in the molecule increases. A better syntan results from condensing a sulfonated and an unsulfonated group rather than condensing two sulfonated groups. A single sulfo group in the naphthalene ring is better than two. The forces between aromatic compounds and protein fibers can be explained by means of electrovalence, dipole affinity and hydrogen bonding; the number of rings in the aromatic molecule and the tendency of coordinating molecules to aggregate are also factors. Attraction between dipoles is the basis of the reciprocal action Both dipole and hydrogen bonds are influenced by electrovalences, sometimes strengthened, sometimes weakened. The above ideas assist in answering the questions of which aromatic compounds have a hydrotropic reaction with collagen, which condensation products will tan, and which dyes will saturate the surface and which will penetrate. I.D.C.

The Anomalous Neutral Salt Effect in the Tanning of Hide Powder with Chromium Chloride-Sodium Chloride Solutions. By A. Küntzel and F. Naumann. *Das Leder* **4**, 201 (1953). The so-called "neutral salt effect" describes the fact that chromium sulfate solutions rich in sodium sulfate do not tan as well (give up less chromium to skin) as liquors that contain little or no sodium sulfate. As a result of this effect partly spent chrome liquors can be regenerated to only a limited extent. Also chrome tanning salts are on the market that are either salt-free or are low in sodium sulfate. On the other hand sodium chloride, especially in chromium chloride liquors, increases take up of chrome. This is called the "anomalous neutral salt effect". The normal effect is the result (a) of a pickling action which decreases swelling and so retards chrome penetration and (b) entrance of sulfate into the chrome complex decreasing its affinity for skin. The anomalous effect, reported by Gustavson [*Ind. Eng. Chem.* **19**, 1015, (1927)], was explained

by him as the result of two opposing factors: (1) an increase in hydrogen ion concentration on addition of sodium chloride, which repressed ionization of the carboxyl groups of the collagen and therefore decreased chrome uptake and (2) entrance of chloride into the chrome complex, which lowered the charge and therefore increased its equivalent weight. The objections to this explanation are that chloride does not enter the complex in chromium chloride solutions of high basicity; also if chloride did enter the complex, it should have the same effect as sulfate. There should be an increase in equivalent weight and an increase in chrome uptake by addition of either chloride or sulfate or a decrease in affinity and decreases in chrome uptake by either. The new theory is that the anomalous effect results from a contact drop and a salting out effect. Chromium chloride is sensitive to sudden increases in basicity. If hide powder is added to a chromium chloride solution which was adjusted to a higher basicity then diluted, the hide powder takes up acid (behaves like an alkali), increases the basicity of the solution, and a highly aggregated basic chrome compound is fixed on the surface of the hide powder. This effect has been noted in commercial practice and was called by P. S. Briggs the contact drop. When the hide and tan liquor come in contact, the liquor concentration drops at once provided there is a great enough difference in acidity between the liquor and hide and if conditions are such that acid withdrawal can cause a substantial rise in basicity. This can occur only if (neutral) hide powder is added in sufficient amount to highly dilute chrome solutions. In concentrated solutions with a large reservoir of acid, the withdrawal of acid by hide powder can play no role. For example, when 3 grams of hide powder were added to 125 cc. of 50% basic chromium chloride, the basicity rose from 50% to 62.5% if the solution contained 5 grams of chromic oxide per liter but only to 51% if the solution contained 50 grams of chromic oxide per liter. Sodium chloride favors aggregation in highly basic chromium chloride solutions. Chloride does not enter the chromium complex, but at high chloride concentrations there is a repression of ionization of the aquo-hydroxo-complexes that results in a salting out. Addition of sodium chloride favors aggregation and aids in deposition of chrome, provided conditions are such that there is a contact drop. A contact drop would not be possible with pickled skin, and the anomalous effect should not be found. Addition of enough sodium chloride to a chromium chloride solution to make it 2 molar in sodium chloride increased the amount of chrome taken up by neutral hide powder but had little effect on the amount taken up by pickled hide powder. The anomalous effect would not be possible with sulfate as it increases the stability of chromium sulfate whereas sodium chloride increases the tendency of chromium chloride to precipitate. I.D.C.

Comparative Investigations on the Influence of Beamhouse Processes and the Tannage on the Area Yield and Properties of Chrome Upper Leather. F. Stather, H. Herfeld and K. Sohre. *Ges. Abhandl. Deut. Lederinsts. Freiberg/Sa.* No. 6, 3 (1951). Twenty-five lots of 10 calf skins each, as nearly alike as possible, were dehaired and tanned in various ways. Post-tanning operations were the same for all lots, except for variations in amount of fat given following certain tannages. Areas, thicknesses, and weights were measured at six different stages, and expressed as percentages of the values found for soaked skins. Chemical analyses and physical tests were made on samples from 3 finished skins from each lot. Each lot was appraised by 5 experienced sorters, and graded separately for fullness, temper and feel, and flanks, on a scale of 1 (best) to 5 (worst), and some lots were awarded premium marks (–) or demerits (+) for other characteristics such as smoothness, looseness, etc. The points for each lot were totalled, and the lots were given overall ratings from 1 (best) to 5 (worst). Similar ratings were given for area, thickness, and weight yields. The standard procedure (lot 1) used for all

lots except as specified, was: *Soak*, 3 days, daily change of water, 30 min. drum wash after 1st day, addition of 0.25% Pekorol L to 2nd, and 0.1% NaOH to 3rd soak. *Liming*, 4 days, in one liquor, starting with 1/3 old liquor and strengthening with 2% hydrated lime, 1% Na_2S (60%) and 0.2% Pekorol FK, at 25-27°C., pulling the skins and warming the liquors on the 2nd and 3rd days, unhairing and fleshing on the 4th day, and returning the skins to the lime liquor for 1 day after unhairing. *Bating*, with $(NH_4)_2SO_4$, Cavit SN, and Creaton 202, at 35°C., for 50 min. *Pickle*, over night, with 150% H_2O, 7.5% NaCl, and 1.5% HCl. *Chrome tannage*, 75% H_2O, 2% NaCl, and 33% basic Cr alum (10% Cr_2O_3 solution) to give 2.5% Cr_2O_3 on skin weight, added in 4 increments over 2 hrs.; after 4 hrs., Na_2CO_3 was added in amount calculated to raise the liquor basicity to 42%, (ignoring pickle acid); after 2 hrs. the skins were piled 2 days, wrung, and shaved. *Neutralizing*, with 2.5% $NaHCO_3$ in 250% H_2O for 1.5 hrs. *Dyeing*, with chrome leather Black E. *Fatliquoring*, with a blend of sulfated neats foot oil, sperm oil, and mineral oil. Subsequent operations followed the usual practice. Lots 2-7 received different unhairing treatments and normal tannage, and lots 8-25 received the normal unhairing treatment and different pickles and/or tannages, as follows: *No. 2*, 4-pit liming, in spent lime, weak $Ca(OH)_2$–Na_2S liquor, used white lime, and fresh white lime successively, 1 day in each, using each liquor for 3 packs. 20°C. *No. 3.* Relimed 4 days in white lime after normal liming. *No. 4.* A 12-day white lime, 6 days in old and 6 days in fresh liquor. *No. 5.* One-day lime with 400% H_2O, 6% hydrated lime, 2.5% Na_2S (60%), and 1% $CaCl_2$, all on soaked weight, at 20°C. *No. 6.* Painted on flesh with paste containing 8% Na_2S plus hydrated lime to give the desired consistency; unhaired after 4.5-5 hrs.; put in white lime over night; fleshed; treated for 30 min. with 400% H_2O and 2% $CaCl_2$, then 24 hrs. in white lime. *No. 7.* Enzyme unhairing, 24 hrs., in drum at 30° with 40% H_2O, 2.5% Arazym IINZ, 1% Arazit 06, and 1%; Arazit 07; unhaired; treated with 400% water and 1.9% Na_2S (60%) for 28 hrs., then with 1% $NaHSO_3$ in 300% H_2O overnight; delimed with 1% $(NH_4)_2SO_4$ and 0.2% HCl in 300% H_2O. *No. 8.* Bating omitted; regular deliming and pickle. No. *9.* Deliming omitted, regular bating and pickle. *No. 10.* Pickled with 2% H_2SO_4; compensating increase in neutralization in tan drum. *No. 11.* No pickle; stock delimed completely at bating. *No. 12.* 25% cut in amount of Cr_2O_3 given; neutralized further till the leather withstood the boil test. *No. 13.* "Dry" chrome tannage with 4.0% Cr_2O_3 in 60% float, and neutralization to 60% basicity; 20% extra fat liquor. *No. 14.* Acid tannage with zero basic chrome alum, neutralized in tan drum to 33% basicity. *No. 15.* Tannage with 33% basic, commercial Cr tanning compound ("Basochrom"). *No. 16.* Tannage with 2.5% Cr_2O_3 in the form of 50% basic Cr chloride, neutralized in drum to 58% basicity. *No. 17.* 2-bath tannage. *No. 18.* Tannage with Novachrome, a commercial Al-Cr tanning compound, 15% basic, containing 5% Al_2O_3 and 10% Cr_2O_3 used 2.5% of the tanning oxides. *No. 19.* Weak CH_3COOH pickle; pre-tannage with HCHO and Lorikal J; regular Cr tannage with 40% cut in Cr_2O_3; 20% cut in fat liquor. *No. 20.* Standard tannage using molasses-reduced Cr liquor. *No. 21.* Pretannage with 1% Cr_2O_3 and 1.3% $Na_2C_2O_4$, on non-pickled stock; then tanned in a fresh liquor with 1.5% Cr_2O_3, normal procedure. No. *22.* Normal Cr tannage; retanned lightly with spruce and syntans. *No. 23.* Normal Cr tannage with 1.5% Cr_2O_3 followed by heavier vegetable retannage; 60% increase in fat liquor. *No. 24.* Straight vegetable tannage with spruce and syntan, 16 days, followed by 2 days' drum retan. *No. 25.* Standard Cr tannage starting with 50% basic Cr liquor. The overall appraisal of these leathers was as follows:

Exper. No.	Nature of experiment	Evaluation Yield			Leather Character	Differences from Standard
		Area	Thickness	Weight		
1	Normal	2	3	4	3	
2	4-pit unhairing	4	5	3	4	
3	8-day liming	5	3	4	2	low strength
4	12-day liming	3	4	4	4	low strength, high porosity
5	1-day liming	5	1	4	1	
6	painted	5	5	4	1	
7	Enzyme unhairing	3	3	2	5	
8	Not bated	3	3	4	2	
9	Not delimed	3	4	5	4	
10	Stronger pickle	4	4	4	3	
11	No pickle	3	4	3	2	very low strength
12	Less Cr.	4	3	4	4	good strength, higher water absorption and porosity
13	Dry Cr tannage	1	4	2	2	better strength
14	Acid pretannage	2	5	3	4	
15	Com. Cr compd.	1	4	3	2	
16	Cr chloride	3	4	3	1	better strength
17	2-bath tannage	2	1	1	2	
18	Cr-Al tannage	2	4	2	2	
19	Cr-Lorikal tannage	4	5	3	4	very good strength very porous
20	Sugar-reduced Cr.	2	5	5	2	
21	Pretannage with oxalate liquor	5	4	3	2	
22	light veg.-syntan retannage	2	2	1	3	
23	Less Cr, heavier retannage	1	1	1	(3)	low porosity very low strength
24	Vegetable tannage	1	2	1	(2)	very low strength very low porosity
25	50% basic Cr liquor	3	4	2	2	

From these tests it appears that a drastic, short unhairing process (No. 5-6) results in low area yield, may or may not give greater thickness yield, and gives highest grade leather.

The dry chrome tannage (No. 13) and the tannage with "Basochrom" (No. 15) gave improved area yield, and the 2-bath tannage gave high yields for both area and thickness. The Cr chloride tannage (No. 16) gave outstanding good leather. High Cr fixation (No.'s 9, 11, 13, 15, 17, 20, 21, 25) had no consistent effect on yield or quality, but abnormally low Cr fixation (No.'s 10, 12, 14, 19) generally resulted in poorer leather and lower yields. The effect of vegetable tannage, or retannage, on the yield is obvious. H. B. M.

The Effect of Finishing with Pigment Finishes and Seasons on the Properties of Shoe Upper Leather. F. Stather and H. Herfeld. *Ges. Abhandl. Deut. Lederinsts. Freiberg/Sa.* No. 6, 24 (1951). The literature is reviewed (36 references). Most publications deal with the properties of the film rather than the physical properties of the leather. Physical tests were made (1) on chrome leather finished on the grain with *(a)* nitrocellulose lacquers, *(b)* water pigment finishes of the Eukanol type, and *(c)* non-pigmented finishes, containing egg albumin, casein, or shellac, and (2) on vegetable upper leather finished on the flesh with a soap-oil season with various proprietary additives. Many series of experiments were made, using one type of finish throughout each series but varying the composition of the finish or the amount applied. Leather from one skin was used throughout each series, so that results within a series are comparable, while results of different series are not. The physical tests showed that none of the finishes had any significant effect on tensile strength, elongation at break, stitch tear and tongue tear strength, or thermal conductivity, and none of the leathers failed after 20,000 flexes. Marked effects were found in absorption of H_2O and permeability to liquid H_2O, air and H_2O vapor. *Nitro-cellulose lacquer finishes*: When the quantity of lacquer was increased from 1 to 3 coats, the H_2O- uptake by Kubelka's method was not affected, resistance to liquid water transmission increased 4-fold, permeability to air was reduced by 92%, and grain-wetting time was increased 5-fold, but permeability to H_2O vapor decreased by less than 10% (note that these are all *static* tests). These properties were affected very little by variation in amount of plasticizer (castor oil + tricresyl phosphate), or in amount and kind of solvent. *Pigment water finish (Eukanol type)*: With increasing amount of finish applied, (from "little" through "medium" to "strong") the effects were qualitatively the same as for the lacquer finish, but less marked. Thus, resistance to passage of liquid H_2O was increased by 150%, air permeability decreased by 92%, permeability to H_2O vapor was reduced by only 6%, and grain-wetting time was increased by about 70%. Quintupling the amount of plasticizer (Eukanol oil) had no effect on these properties, nor did tripling the dilution of the applied finish, nor after-spraying with 10% or 25% HCHO solution, though the HCHO, of course, improved the fastness to wet rubbing. *Non-pigmented grain finish*: In tests using dyes plus egg albumin, casein + NH_3, or shellac + NH_3, each binder being used separately, the water uptake in 2 hrs. was about 10% greater, and the grain-wetting about 50% shorter, for the leathers finished with casein or shellac, compared to leather finished with albumin, probably because the former were dissolved in ammonia. Permeabilities towards liquid H_2O, air, and H_2O-vapor were the same for all. The effect of amount of albumin was studied by comparing leathers with no finish, "'normal" finish, and 2.5 times the normal amount of finish. Application of the normal finish did not affect H_2O-uptake, increased the grain-wetting time 6-fold, increased the resistance to liquid water transmission by 35%, reduced air permeability by 50%, and reduced H_2O vapor permeability by 10%. The 2.5 normal application further reduced the permeability to air and liquid water, and further increased the grain-wetting time, with only a light effect on H_2O vapor permeability. *Flesh finish*: This finish contained tallow 10, degras 10, train oil 20, and curd soap 5 parts, in 100 parts water. Application of the normal quantity to the flesh of "Fahl-

leder" reduced H_2O-uptake (24 hrs.) by about 15%, increased flesh-wetting time by 11%, increased the resistance to passage of liquid water by 53%, reduced air permeability by 23%, and reduced H_2O vapor permeability by only 4%, all compared to non-finished leather. Application of 3 times the normal quantity enhanced all these effects about as expected. Addition to the finish of Colloresin DK or Hortol S 25 greatly reduced the permeability to air and to liquid H_2O, and reduced the H_2O-uptake in 2 hrs., but not in 24 hrs., without affecting permeability to H_2O vapor. Hortol S 25 had a greater effect than Colloresin DK.

H. B. M

Investigation on Fur Dressing and Fur Improvement. V. Color Lake Formation During Dyeing of Hair with Oxidation Dyestuffs. F. Stather and R. Schubert. *Ges. Abhandl. Deut. Lederinsts. Freiberg/Sa.* No. 6, 50 (1951). Furs are often dyed with p-amino-phenol ("Ursol P" or other trade names), p-phenylenediamine ("Ursol D"), aniline ("Ursol-Black Oil"), and similar compounds that are oxidized on the hair by H_2O_2 in the presence of metal mordants. Experiments to determine the effect of variable conditions on dye penetration were made, using a 15% gelatin gel as model substance. A 10-mm. layer of gelatin was treated with 10 ml. of solution (mordant, dye, or oxidizing solution, alone or in various successions), and depth of penetration was measured after 24 hours. Mordants studied were $K_2Cr_2O_7$, $CuSO_4$, $FeSO_4$ and $K_2SO_4 \cdot Al_2(SO_4)_3$. In tests with mordant only, $K_2Cr_2O_7$ penetrated twice as well as the Cu, Fe, and Al mordants. Penetration of each increased, but not linearly, with concentration (0.25-2.5 g. per liter). pH value had little effect (2.0-5.0) except with $FeSO_4$ and alum at the higher pH values where precipitation occurred. Deeper penetration took place when the gel was treated with the dye (Ursol D) first, followed by the mordant, than when this order was reversed. The effects of order of treatment was most marked for Fe, and least for Cu. When the gel was treated 24 hours with mordant solution (0.25 - 2.5 g. per liter), and then 24 hours with 10 ml. Ursol D solution (2 g. dye + 2 ml. 30% H_2O_2 per liter), penetration decreased with increasing concentration of $K_2Cr_2O_7$, but increased with increasing concentration of the Cu, Fe and Al mordants. Variations of pH value of mordant (2-5) had practically no effect on subsequent penetration of dye. The effect of varying H_2O_2 concentration (0.5-5.0 g. per liter) depended on the mordant. With $K_2Cr_2O_7$, penetration decreased, and with alum penetration increased with increasing H_2O_2; with $CuSO_4$ penetration was constant, and with $FeSO_4$, penetration increased, up to 2 g. per liter H_2O_2, and was lower with 5 g. per liter H_2O_2 for both $CuSO_4$ and alum. Penetration increased with amount of dye (Ursol D), but the amount of the increase varied greatly with the mordant. For $K_2Cr_2O_7$, penetration was 5 times as great with 5 g. Ursol D per liter as with 0.5 g., while this 10-fold increase in dye merely doubled the penetration with the other mordants. The specific effect of kind of mordant was different for different dyes (Ursols). Thus Ursols D, DF, and A (2 g. dye + 2 ml. H_2O_2 per liter), on gelatin treated with 0.1% mordant, differed little in penetration, among themselves or with different mordants, but Ursol P gave a much lower penetration with Cr and Al, and Ursol F a much lower penetration with Fe mordant. Color lake formation was studied by mixing solutions of Ursol D with the various mordant solutions, filtering, washing, weighing, and analyzing these precipitates for the metals concerned. The quantity of precipitate increased with quantity of mordant (Ursol D and H_2O_2 constant) for all 4 mordants up to 1 g. per liter. Further increase, to 2.5 g. per liter, caused a further increase in precipitate with Cr and Cu, no change with Fe, and a decrease with Al. The weight of precipitate obtained with different mordants, at any one concentration, decreased in the order Cr, Cu, Fe, Al, but the % of metal in the precipitate decreased in the order Fe, Al, Cu, Cr at low mordant concentrations, and Fe,

Cr, Al, Cu at high mordant concentrations. Amount of precipitate increased, but % metal in the precipitate decreased, with increasing concentration of H_2O_2, for all mordants. The amount of precipitate increased with Ursol D concentration, but the percentage of total dye that was precipitated decreased, and so did the % metal in the precipitate. In tests with 5 different Ursols, the order of amounts of precipitate obtained with different metals was the same for all, but the percentages of the different metals in the precipitate varied with the dye. Dyeing tests were made on wool and rabbit hair, previously defatted, and treated with Na_2CO_3 and NH_4OH. The hair was treated for 24 hrs. with the mordant solution, and then 24 hrs. with the dye, with addition of H_2O_2 after 1 hr. This order of treatment gave a more uniform dyeing than the reverse order. With wool, the intensity of color increased with concentration of mordants but the feel was impaired. Wool mordanted with $K_2Cr_2O_7$ had the mildest feel. Shades were different for the different mordants, and different for wool and rabbit hair. Varying the pH value had no effect. Intensity of shade increased with concentration of Ursol D to a maximum at 2 g. per liter (= 2 g. per 10 g. hair). Increasing the amount of H_2O_2 (30%) above 2 ml. per liter had an unfavorable effect on wool, and no effect on hair. The shades produced were specific for the different Ursols and for the different mordants. The % metal in hair or wool increased with the amount of mordant used—linearly for Cr, and to a much smaller degree with Cu, Fe, and Al. Percentage of metal in wool decreased with increasing pH value, and with increasing H_2O_2 concentration. The tensile strength of hair and wool decreased slightly, and elongation at break decreased considerably, with increasing concentration of mordant and H_2O_2 employed. H. B. M.

Microscopic Investigation of Bleaching and Dyeing Processes in Fur Upgrading. Fritz Stather. *Ges. Abhandl. Deut. Lederinsts. Freiberg/Sa.* No. 8, 3-11 (1952); see preceding abstract. The microstructure of rabbit hair is described (illustrated). The medulla of white rabbit hairs is almost completely destroyed by 2 hr. treatment with 2% NaOH ("killing"), without visible alteration of the cortex. Destruction of the medulla of black hairs is less complete. After successive treatment of black rabbit hairs with (1) 0.2% Na_2CO_3 + 0.01% NH_3 for 1 hr., (2) 1% $FeSO_4$ for 12 hrs., and (3) 1% H_2O_2 at pH 8.2 for 2 hrs., the pigment granules of the medulla are largely destroyed while those of the cortex are intact. After 12 hr. treatment with H_2O_2, the cortex pigment are changed from blue to yellowish. White rabbit hairs treated with 0.2% Na_2CO_3 + 0.01% NH_3, and then with Ursol D + H_2O_2 for 24 hrs. (no mordant), showed a light, blue-violet color throughout most of the cortex but generally not reaching the medulla. The same dyeing after pretreatment with NaOH, followed by $Na_2Cr_2O_7$, gave an intense color throughout the cortex. Dyeing tests with thin, white wool hairs, that show no medulla, showed that penetration and intensity of color can be varied by mordanting, as follows: 0.25% $K_2Cr_2O_7$, complete penetration, pale color; 2.5% $K_2Cr_2O_8$, one-third penetration, intense color; 0.25% - 2.5% $FeSO_4$, complete penetration, pale color; 0.25% $CuSO_4$, surface dyeing, intense color; 2.5% $CuSO_4$, complete penetration. Pickling and tanning operations had no visible effect on the microstructure of the hair, but tannage with Cr or Al resulted in slightly deeper shades after dyeing. H. B. M.

The Question of Scalding of Pig Skins. Fritz Stather. *Ges. Abhandl. Deut. Lederinsts. Freiberg/Sa.* No. 8, 12 (1952). Hausam [*This Journal* **43**, 756 (1948)] claimed that

pigs can be dehaired by scalding without damage to the hide, if the temperature is held between 59 and 62, or 63°C., and the scalding time is the minimum for satisfactory dehairing (2.5 - 7.5 min.). This so-called "Dresden process" apparently works well in the Dresden slaughter houses, but not elsewhere, perhaps owing to poor temperature control. Data are presented that shows that pig skin is damaged by exposure to water at 57.5° and above —the extent of the damage increasing with temperature, and with time of exposure (2.5- -10 min.) at 60°. Those data include percentage of total collagen dissolved in the hot water and during subsequent bating, and tensile strength and stretch measurements made immediately after the hot water treatment, after bating, and on chrome-tanned leather. These laboratory experiments were supplemented by tensile strength and stretch measurements on comparable lots of pig suede leather, dehaired by the Dresden scalding process or without scalding. The leather from the scalded skins, though not visibly damaged, was 15% lower in tensile strength, and 6% lower in elongation at break, than the non-scalded skins. The extent of damage indicated by laboratory tests was considerably greater than this. The practice of scalding is condemned. H. B. M.

The Evaluation of Synthetic Replacement Tannins. F. Stather and H. Herfeld. *Ges Abhandl. Deut. Lederinsts. Freiberg/Sa.* No. 8, 21 (1952). The leather-forming properties of numerous syntans prepared in the laboratory [*This Jour.* **48,** 322 (1953)], are compared with results of analytical determinations, to see which determinations are most valuable for predicting tanning power. Combining value ("Bindungswert") [*This Jour.* **47,** 629 (1952)] is the best analytical evidence of tanning power. Out of all the compounds that showed unquestionable tanning properties by laboratory tanning tests, 80% had combining values of 30 or higher, while 88% of the compounds of doubtful tanning power, and 98% of the compounds that had no tanning value, gave combining values below 30. No such distinction could be made on the basis of tannin content, purity, tan value ("Gerbwert"), or salt precipitation value [*This Jour.*, **47,** 630 (1952)]. Combining value measured with cow hide splits, or with calf skin in 2 $cm.^2$ pieces, correlated less well with leather-forming properties than did combining value determined with hide powder (24 hrs. contact). Other determinations give useful information, even though they do not afford a sound basis for predicting leather-forming value. Determinations of rates of fixation and penetration [*This Jour.*, **47,** 664 (1952)] are useful if parallel determinations are made with tannins of known tanning rate. Analytical tannin content is determined solely to eliminate compounds that are obviously worthless, and to permit a calculation of the quantities to be used in tanning tests. Tannin should be determined in 0.4% solution, or, if this solution is not completely detanned, then in the strongest solution that can be completely detanned. A purity of 60% is desirable, to avoid excessive accumulation of non-tannins, but many compounds of lower purity tan well. Apparently purity should vary little with concentration in the range 0.25 - 0.40% tannin. More than 10% ash is undesirable, because of the adverse effect on purity, and because of possible salting out of vegetable tannins generally used along with syntans. Insoluble matter should not exceed 5%, at analytical dilution, or 3% by volume in a centrifuged solution containing 5% tannin. For most compounds of unquestionable leather-forming properties, the fraction of tannin precipitated by 1/3- saturated NaCl exceeded 30%, and the fraction precipitated by saturated NaCl exceeded 60%. A tan value ("Gerbwert") exceeding 50 (24 hrs.) is desirable but not essential. Other recommended tests include: pH value (analytical dilution) 3.5 or higher; difference figure 0.7 or higher; Fe_2O_3 not over 0.1%, preferably 0.05%; CaO not over 1%, preferably 0.5%; free phenol absent. H. B. M.

PATENTS

Sulfite Waste Liquor Extract Rich in Tanning Matters and Poor in Ash and Salts. Ger. Pat. 863,983. Zellstofffabrik Waldhof. Jan. 22, 1953. Through *Chem. Abst.* **47**, 6142 (1953). The known process of preparing sulfite cellulose waste liquor extracts by neutralization, evaporation, and precipitation with suitable acids to remove calcium ions is improved by treating the waste liquor before evaporation with liquid or gaseous NH_3 until the neutralization point is reached or slightly exceeded, preferably at elevated temperature. The quantity of the precipitative acid should be selected so as to effect a complete precipitation of the present Ca ions as insoluble salt and to set free the lignosulfonic acid. Thus, gaseous or liquid NH_3 is added to 1 cu. m. of 60° Bé. unfermented waste liquor until the latter shows no acid reaction to litmus. The liquor is evaporated up to 30° Bé and then triturated with a mixture of equivalent quantities of $(CO_2H)_2$ and H_2SO_4 diluted with the same amount of water until the Ca compounds are practically completely precipitated. The precipitate is removed, and the solution of pure lignosulfonic acid can be used for tanning purposes. On dry basis it contains about 74 per cent tanning matters, 2.9 per cent ash, and 4.5 per cent inorganic salts.

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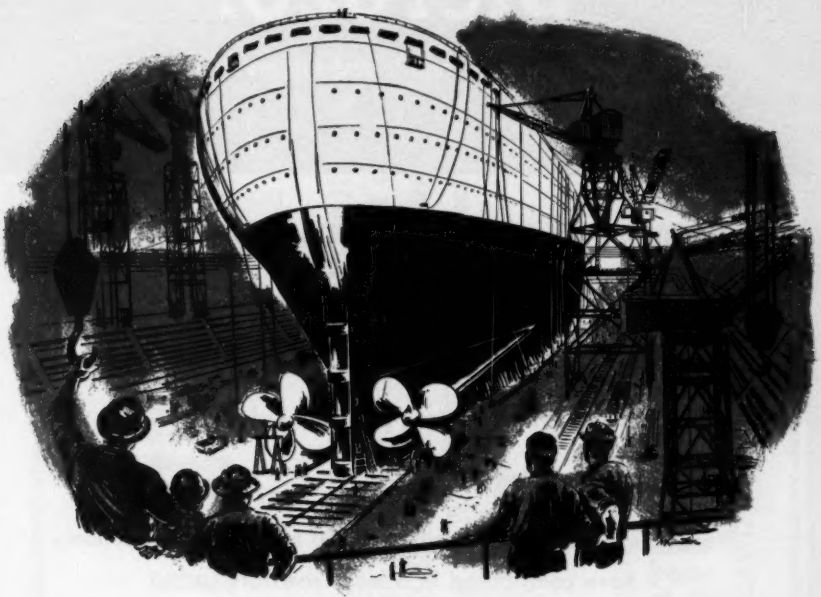

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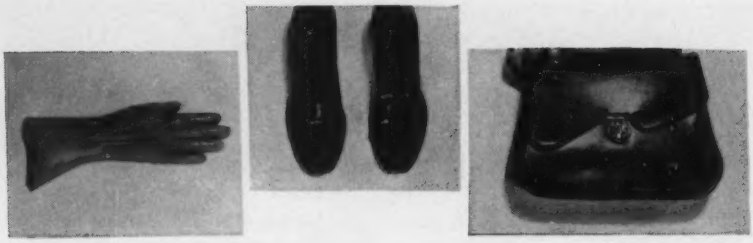

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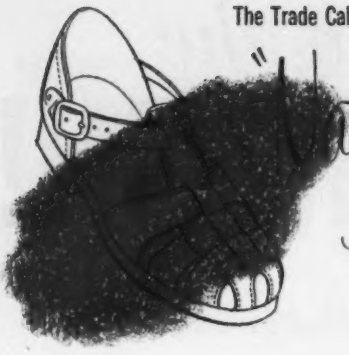

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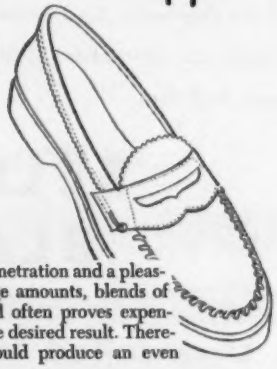

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